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Vol. 31. No. 260. August 1945.

THE PRECISION AND ACCURACY OF VISCOMETRY USING B.S.I. TUBES.

By The Viscosity Panel of Standardization Sub-Committee No. 6—Lubricants.

At the First World Petroleum Congress held in London in 1933 a resolution was adopted that viscosities should preferably be expressed as kinematic viscosities, and that international co-operation was necessary to ensure that the same values of units of kinematic viscosity are in use in different countries.

A comparison of the unit of kinematic viscosity—the centistoke—is a matter of considerable difficulty, as there is no certainty that oils will retain their viscosity unchanged under different storage conditions. Dr. Barr has long felt that international standardization of viscosities should be made with viscometers of known characteristics, as these are much less likely to change than standard viscosity oils.

At a meeting of a Panel of the International Association for Testing Materials at the First World Petroleum Congress, it was arranged that two glass U-tube viscometers, numbers 2 and 3, conforming to the British Standard Specification No. 188 of 1929, should be calibrated in a number of the national standardizing or associated laboratories. The same instruments were circulated to the following laboratories.

(1) The National Physical Laboratory, Teddington.
(2) Physikalisch-technische Reichsanstalt, Berlin-Charlottenburg.
(3) Ecole Nationale Superieure du Petrole, Strasbourg.
(4) Professor Bingham, Lafayette College, Easton, Pa.
(5) Dr. R. N. J. Saal, Laboratorium van N. V. de Bataafsch Petroleum Maatschappij, Amsterdam.

Different methods of calibrating were used in each laboratory, but the methods of test were those laid down in the British Standards Specification. Calibration constants obtained were not reported until 1937, as there was considerable delay in the circulation of the instruments from one laboratory to another. The absolute values of the constants reported by the five laboratories differed in some cases by more than ± 2 per cent. from the mean, and further absolute and comparative experiments were therefore required before satisfactory agreement could be reached on practical standards of kinematic viscosity.

In the meantime, the standardization of methods of test was transferred to the International Standards Association and its Sub-Committee 28 A/18.

At a meeting held at Brussels, 26th–28th January, 1939, at a conference on viscosity measurements, it was agreed that the Institute of Petroleum should order a number of Ostwald viscometers B.S.I. Nos. 2 and 3, which would be calibrated by the National Physical Laboratory and then supplied to the countries participating in the tests. Arrangements were made simultaneously to supply a set of samples of three oils, described as

Oil 38, Oil 25, and Oil 39, prepared by the laboratory of the Bataafsch Petroleum Maatschappij, of which two oils were to be run on each instrument; the viscosities were about 17, 80, and 530 centistokes at 20° C. Great care had been taken in the preparation of the oils, and it was recommended that they should be kept in the dark in a cool, dry place until the viscosity determinations were made. No less than fourteen laboratories in the United States, Sweden, Denmark, Germany, France, Holland, and England had arranged to take part in these tests, and all these laboratories were to determine flow times in the viscometers supplied to them on the same dates. At the same time the oils were also to have their viscosities determined, by those national standardizing bodies taking part, in their own instruments. The arrangements for these tests were made by the Institute of Petroleum Viscosity Panel, and a series of thirty-two viscometers, sixteen of No. 2, 145/9 to 160/9 inclusive and sixteen of No. 3, 129/9 to 144/9 inclusive, were sent to the N.P.L. for calibration. The flow times of two other oils of different viscosities at 25° C. were observed by the N.P.L. in each of thirty-two tubes, and the results were not communicated to any of the participants. Times were determined in triplicate and mean values were deduced: the readings agreed with $\pm 0{\cdot}1$ per cent.

It had been arranged that the whole of the results should be sent to the N.P.L. and, when completed, should be examined and reported upon by the Institute of Petroleum Viscosity Panel, but owing to the Second World War, only a few of the laboratories taking part returned their test results. It was, however, felt that some account of the work should be given as a record of what progress has been made.

The N.P.L. constructed a table giving the ratios of the mean flow times in each of the viscometers of range 3 to the mean flow times of the same oils in relation to one viscometer No. 140/9, and of the mean flow times in each viscometer of range 2 to those in viscometer No. 150/9. This table is presented here as Table I. The oils had viscosities, measured in N.P.L. standard tubes at 25° C. as follows (June 1939) :—

Oil A	122·7 cs.
Oil 200	41·3 cs.
Oil 40	5·15 cs.

It is stated that Oil 40 was calibrated in a No. 2 tube (40 per cent. sucrose) which gave the viscosity of an oil (No. 25) as 78·93 cs. when its viscosity in a No. 3 tube (60 per cent. sucrose) was 78·63 cs. Thus Oil 40 may possess a viscosity of 5·14 cs. based on 60 per cent. sucrose. The other two oils were calibrated in a No. 3 tube using 60 per cent. sucrose solution.

All the tubes, except Nos. 140/9 and 150/9, were then despatched in pairs to different laboratories both in Europe and in the U.S.A. Nos. 140/9 and 150/9 were retained at the N.P.L. The viscosities of the three oils supplied to each laboratory were determined by the N.P.L. (October 1939) :—

Oil 38	viscosity at 20° C. . . .	17·75 cs.
Oil 25	viscosity at 20° C. . . .	78·63 cs.
Oil 39	viscosity at 20° C. . . .	526·0 cs.

TABLE I.

Oil A in tube No. 140/9. 485·2 sec.
Oil 200 in tube No. 140/9. 163·4 sec.
Oil 200 in tube No. 150/9. 909·2 sec.
Oil 40 in tube No. 150/9. 113·1 sec.

Range 3. Relative Flow Time.			Range 2. Relative Flow Time.		
Instr. No.	Oil A.	Oil 200.	Instr. No.	Oil 200.	Oil 40.
129/9	0·8884	0·8915	145/9	0·8544	0·8540
130/9	0·8811	0·8861	146/9	0·7795	0·7796
131/9	0·8855	0·8881	147/9	0·8838	0·8821
132/9	0·9237	0·9262	148/9	0·8935	0·8925
133/9	0·8652	0·8669	149/9	0·9774	0·9777
134/9	0·9353	0·9397	150/9	1·0000	1·0000
135/9	0·9449	0·9469	151/9	0·7850	0·7857
136/9	1·0268	1·0284	152/9	0·7986	0·7980
137/9	0·9536	0·9543	153/9	0·9236	0·9221
138/9	1·0648	1·0670	154/9	0·8683	0·8675
139/9	0·9768	0·9763	155/9	0·7664	0·7669
140/9	1·0000	1·0000	156/9	0·7155	0·7129
141/9	0·8913	0·8930	157/9	1·0389	1·0403
142/9	0·8556	0·8581	158/9	1·0070	1·0053
143/9	0·8822	0·8835	159/9	1·0168	1·0177
144/9	0·9100	0·9124	160/9	0·9918	0·9928

TABLE II.

Tube No.	Oil No.	Time of Flow, secs. at 20° C.	Laboratory.	Date.
135/9	25	291·7	France (Université de Strasbourg).	—
135/9	39	1974·1		
146/9	25	1336·8		
146/9	38	301·8		
129/9	25	292·0	Denmark (Association Danois de Standardisation).	—
129/9	39	1950·7		
160/9	25	1361·7		
160/9	38	305·4		
144/9	25	282·9	Stand. Inspection Labs. U.S.A. (Esso).	Nov. 1939
144/9	39	1892·0		
148/9	25	1545·0		
148/9	38	347·4		
140/9	25	311·0	N.P.L.	Oct. 1939
140/9	39	2071·3		
150/9	25	1731·6		
150/9	38	389·1		
141/9	25	277·0	Esso European Labs.	—
141/9	39	1859·0		
145/9	25	1482·6		
145/9	38	332·4		
130/9	25	277·0	Burmah Oil Co.	Jan. 1940
130/9	39	1850·5		
159/9	25	1774·0		
159/9	38	395·5		

Oils 25 and 39 were tested in a No. 3 tube calibrated by 60 per cent. sucrose. Oil 38 was tested against 40 per cent. sucrose in a No. 2 tube

and, similarly to Oil 40, may therefore have a viscosity of 17·71 cs. against 60 per cent. Not all the laboratories have been able to return test results, as the work was initiated in 1939. Table II gives the results available. Certain of these laboratories further gave viscosity values for these oils at 20° C. as measured by their own viscometers. All figures given are for a temperature of 20° C. These figures are given in Table III. These three tables comprise all the data available from these tests.

TABLE III.

Laboratory.	Viscosity of Oil at 20° C.,			Remarks.
	Oil 25.	Oil 38.	Oil 39.	
N.P.L.	78·63	$17{\cdot}7_{1-5}$	526·0	October, 1939.
U.S.A.				
Stand. Insp. Laboratory	79·00	17·77	528·7	A.S.T.M. suspended level (Nov., 1939).
Penn. State	78·89	17·76	527·6	Fenske-Cannon.
National Bureau of Standards	79·08	17·79	528·5	Bingham and Pyknometer.
Denmark (Assoc. Danois de Stand.)	77·92	17·47	521·0	Raaschour Viscometer.
Esso European Laboratories	78·77	17·70	527·0	N.P.L. Calibrated Ostwald.
Texas Oil Co., Ltd.	—	17·65	529·8	Company's Master Ostwald tubes.

ANALYSIS OF ERRORS AND PRECISION.

It was found that Table I does not represent the best way of presenting the results. All times recorded are divided by the times of flow of the same oils in two arbitrarily chosen tubes, 140/9 and 150/9, of which the accuracy is unknown. The ratio of the times of flow of two oils in the same tube was therefore calculated, and Table IV gives the ratio for different tubes which are also presented on Figs. 1 and 2.

As precision in the time reading was reported to $\pm$ 0·1 per cent., it is obviously useless to specify a higher precision on the agreement between the different tubes. If $\pm$ 0·1 per cent. be made the maximum allowable divergence from the mean value, it will be seen from Figs. 1 and 2 that in both cases a number of tubes, just over half the total, give results within these limits. The maximum divergence for all tubes in both series is of the order of $\pm$ 0·3 per cent. from the mean value.

Two important conclusions follows :—

(1) It is possible to limit the maximum error to $\pm$ 0·1 per cent. from the mean value in measuring the viscosity of an oil 2 by means of U-tube viscometers of the B.S.I. type which have been calibrated by means of an oil 1, if a number of such tubes are first subjected to a simple quality-control test. This quality-control test consists of finding the ratio of the time of flow of at least two oils in a number of tubes, rejecting all tubes

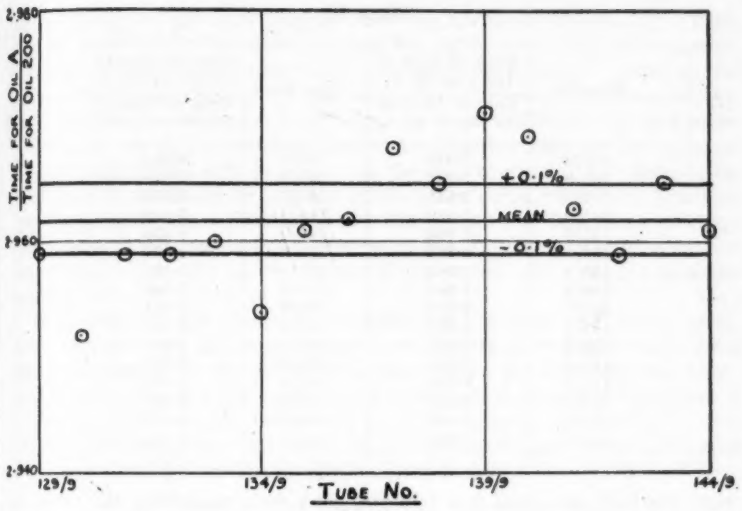

FIG. 1.

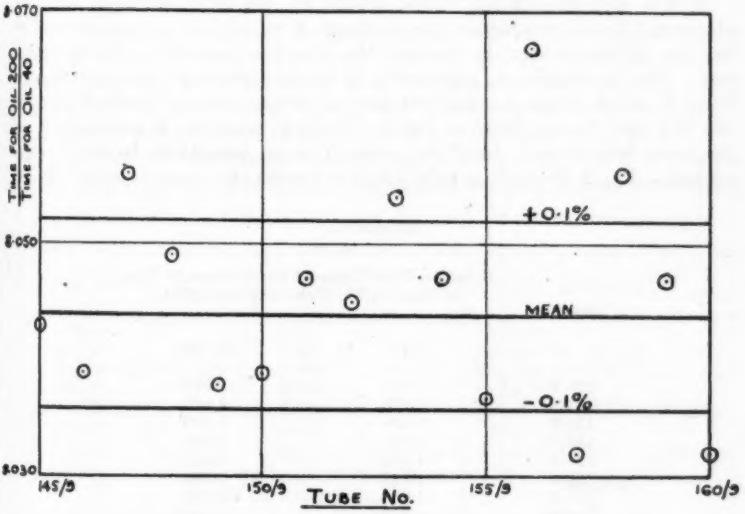

FIG. 2.

giving a divergence from the mean exceeding $\pm 0{\cdot}1$ per cent. and retaining the rest. This conclusion implies that the excessive divergence is due to imperceptible faults in the tubes, and not in the procedure. This implication is justified, as all the tubes were subjected to the same procedure and gave repeatable results in the same laboratory. It appears

TABLE IV.

Tube No.	Time of Flow of Oil A at 25° C. / Time of Flow of Oil 200 at 25° C.	Tube No.	Time of Flow of Oil 200 at 25° C. / Time of Flow of Oil 40 at 25° C.
129/9	2·959	145/9	8·043
130/9	2·952	146/9	8·039
131/9	2·959	147/9	8·056
132/9	2·959	148/9	8·049
133/9	2·960	149/9	8·038
134/9	2·954	150/9	8·039
135/9	2·961	151/9	8·047
136/9	2·962	152/9	8·045
137/9	2·968	153/9	8·054
138/9	2·965	154/9	8·047
139/9	2·971	155/9	8·037
140/9	2·969	156/9	8·067
141/9	2·963	157/9	8·032
142/9	2·959	158/9	8·056
143/9	2·965	159/9	8·047
144/9	2·961	160/9	8·032

that this test, an actual flow test and not merely subjecting the tubes to dimensional specifications, should be the final check for tubes for accurate viscometry.

(2) For well-constructed tubes, tested by the dynamic test outlined above and found acceptable, the constant of calibration is independent of the time of flow within the limits of the precision imposed in the dynamic test. This conclusion is apparently in contradiction of the evidence in Table I, which shows a consistent increase in the ratio of times of flow of oils in a tube to the times in 140/9. Table I, however, is misleading, as the basic tube chosen, 140/9 for range 3, is an unsuitable basis of comparison. Fig. 1 shows that tube 140/9 is among the worst rejects. Tube

TABLE V.

Tube No.	Relative Flow Times of Oil in Tube to Time of Same Oil in Tube 133/9 at 25° C.	
	Oil A.	Oil 200.
129/9	1·027	1·028
131/9	1·023	1·024
132/9	1·068	1·069
133/9	1·000	1·000
135/9	1·092	1·092
136/9	1·187	1·186
141/9	1·030	1·030
142/9	0·9891	0·9895
144/9	1·052	1·052

150/9 is just on the border-line. It will be seen that for range 2—*i.e.*, where the basis of comparison (150/9) is acceptable—the ratios of times in Table I differ both on the positive and negative side of the mean by small amounts. The maximum divergence is for tube 156/9, giving 0·003

in 0·715 or 0·4 per cent. higher value for the more viscous oil. Tube 156/9, however, is the worst among the tubes tested by the dynamic quality-control test just described, and would be rejected. None of the tubes of range 2 accepted by this dynamic test shows more than 0·1 per cent. difference in the ratio from the mean value of the two oils, and these differences are not consistently in favour of either high or low rates of flow for eightfold range in rates. In the case of range 3 the tube to be used as a basis should be any one of the tubes which passed the dynamic quality-control test. Probably tube 133/9 gives the best basis of comparison, as it falls on the exact average in Fig. 1. Thus Table V gives the appropriate data for all the tubes which passed the dynamic quality-control test.

It is seen that the change in the ratio is of the order of 0·05 per cent. from the average, and even though more results show higher ratio with the more viscous oil, the deviation is below the 0·1 per cent. precision limit, and thus is without significance. It is interesting to note that by correctly choosing 133/9 and not 140/9 as a standard tube, even tubes 139/9 and 140/9 (the two giving the worse results on the dynamic quality-control test) give the following reasonably constant ratios :—

Oil.	Ratio for Oil A.	Ratio for Oil 200.
139/9	1·129	1·126
140/9	1·155	1·153

The deviation, however, is such that a lower-calibration constant is obtained with the more viscous oil. Thus it is concluded that the calibration constant for tubes which pass the dynamic quality-control test is independent of the time of flow of the calibrating oil for both range 2 and range 3 tubes and for ratios of viscosity of oils used up to 8 : 1.

The above two conclusions combine into the corollary that it is possible to find the viscosity of an oil, 3, by means of stepping-up procedure using

TABLE VI.

Tube No.	Ratio of Flow Time of Oil 39 at 20° C. to Time of Oil 25 at 20° C.	Remarks.
129/9	6·681	Denmark.
130/9	6·681	Burmah Oil Co.*
135/9	6·768	France.
140/9	6·660	N.P.L.*
141/9	6·711	Esso European Laboratories.
144/9	6·688	Esso., U.S.A.
Tube No.	**Time of Oil 25 at 20° C. to Time of Oil 38 at 20° C.**	**Remarks.**
145/9	4·460	Esso European Laboratories.
146/9	4·429	France.
148/9	4·447	Esso., U.S.A.
150/9	4·450	N.P.L.
159/9	4·486	Burmah Oil Co.
160/9	4·459	Denmark.†

* Tube is reject on Fig. 1. † Tube is reject on Fig. 2.

two other oils, 2 and 1, and two U-tubes of the B.S.I. types to within $\pm 0{\cdot}2$ per cent. maximum error from a mean value, provided that both tubes have passed the dynamic quality-control test and that the experiments are performed in the same laboratory and at one temperature. It is to be noted that nothing in Table I or the better conversions Tables IV and V can give assurance that the calibration constant is not influenced by the temperature of the bath or the particular laboratory and country of test. Unfortunately, nothing in this work can be used to evaluate the influence of temperature on the calibration constant. However, Tables II and III may be analysed for the discrepancies in viscosities reported by different laboratories. The dynamic quality-control test is applied to the contents of Table II to find the discrepancies between laboratories using the same oils and different tubes.

Table VI gives the results for all the laboratories. It is evident that the results from France disagree from all others and can be neglected until a more detailed study of the causes of difference can be realized. When neglecting the French results as well as those obtained with tubes which are unsuitable for accurate viscometry, the discrepancies between the different laboratories using good tubes reach a maximum of $\pm 0{\cdot}25$ per cent. from the mean for all laboratories for range 3 tubes and $\pm 0{\cdot}7$ per cent. for range 2 tubes. As samples of the same oils were tested at approximately the same date in tubes which have yielded good results in a single laboratory, it becomes apparent that there is need to study the factors which make laboratories differ so much from each other. It is to be remembered, however, that for most purposes, the calculation of V.I. included, tests would normally be done in a single laboratory.

Accuracy of Viscometry.

Table III affords a possibility of studying the accuracy of viscometric methods used. (Not all the laboratories which returned results tabulated in Table II returned viscosity values.) It is evident that the Danish viscometric method gives low values when compared with British and U.S.A. methods. Results from the Texas Oil Co., Ltd., show a relatively larger difference from the mean British viscometric results than either of the two others, hence for a first comparison they are excluded. The N.P.L. and Esso European Laboratories agree to within 1 in 800 maximum difference. As both results are based on N.P.L. calibration, this is not great significance from the view-point of accuracy. The U.S.A. results use three distinct methods, and the agreement between the three results is to within 1 in 500 maximum difference giving $\pm 0{\cdot}1$ per cent. deviation from the mean. The averages for the U.S.A. and British results (excluding the Texas Oil Company's results) are as follows.

If we take the average results for British values for all three laboratories concerned we obtain :—

Oil . . .	25	38	39
Viscosity, cs. .	78·70	17·69	527·3

This gives deviations of $+0{\cdot}36$, $+0{\cdot}45$, and $+0{\cdot}19$ per cent. The average deviation is 0·33 per cent.

TABLE VII.

	Viscosity of Oil at 20° C., cs.		
	Oil 25.	Oil 38.	Oil 39.
U.S.A.	79·09	17·77	528·3
British	78·70	17·71	526·5
Diff. = U.S.A. − British . .	+0·29	+0·06	+1·8
% diff. = $\frac{\text{diff.} \times 100}{\text{mean}}$ . .	+0·36	+0·34	+0·34

Thus, it appears either differences in the fundamental scales of the dimensions mass, length, and time and of temperature as used in the two countries may exist giving unidirectional errors or the practical units of viscosity used in the two countries may be different. The basis of the American unit is the viscosity of pure water at 20° C., that in Britain is the viscosity of 60 per cent. sucrose at 25° C. It is to be noted that the N.P.L. adopted the 60 per cent. sucrose as standard on the basis of Dr. Barr's experiments in which he has shown deviations between different absolute methods amounting to 0·3 per cent. Viscosity results calculated on a basis of calibrating with a 40 per cent. sucrose would make the British and American results agree to less than 0·1 per cent. error. Other work, however, has shown the 40 per cent. sucrose viscosity to be unreliable as a standard.

CONCLUSIONS.

(1) It is not satisfactory to rely solely on the present dimensional specifications for B.S.I. tubes if viscosities are to be determined with ± 0·1 per cent. maximum error from a mean value for results obtained in different laboratories using the same basis for the practical unit.

(2) In any one laboratory agreement in viscosity determinations within 0·2 per cent. can be obtained if the ratio of times of flow of two oils are determined in the tube under test in comparison with a tube shown to be satisfactory in a dynamic control test outlined above, such that the ratio of time of flow of two oils is within ± 0·1 per cent. of the mean of a large number of tubes (15–20).

(3) In any one laboratory, tubes calibrated by the procedure under No. 2 above can be used for stepping-up viscosities and should give agreement with ± 0·2 per cent.

(4) Further investigation is required to obtain closer agreement between different laboratories and particularly as regards :

(*a*) temperature measurement, and
(*b*) time measurement.

(5) Viscosity measurements in the U.S.A. by fundamentally different methods, on the same oil show maximum differences of ± 0·12 per cent. from the mean value.

(6) British mean values of viscosities on these oils are 0·35 per cent. below the mean values obtained in the U.S., suggesting that the fundamental unit of centistokes has a different practical value in the two countries.

THE TESTING OF GREASES FOR BALL-BEARINGS.*

By S. R. Pethrick, B.Sc.

Summary.

Conventional methods for testing greases are of little assistance in the selection of greases for particular applications.

Tests on lime-base greases should include: (1) flow measurements at various rates of shear and at various temperatures, (2) an oxidation test with an examination of the oxidation product, and (3) a syneresis test involving capillary action.

Soda-base and lithia base greases vary widely in texture, cohesion, and adhesion; and some method of measuring these properties is desirable. The combined cohesion and adhesion properties can be examined by measurements of the torque exerted on the housing of a rotating bearing, when the latter is partially filled with grease. A suitable apparatus for torque measurements is described.

A churning test followed by torque measurements gives useful information on the stability of a grease.

In recent years the Institute of Petroleum has endeavoured to achieve a high degree of standardization of the methods for testing petroleum products.

The methods so far standardized for testing lubricating greases are of value for the routine checking of a particular product, but the results of such tests do not render it possible to select a grease for a particular application without a full-scale test in the equipment to be lubricated.

It is well known that a number of greases giving the same penetration value can be made by compounding a soap with a number of oils of varying viscosities, and similarly, by incorporating a number of different soaps in an oil, several products having the same consistency can be produced.

It is extremely unlikely that all the products made by the various methods will give similar performances in lubricating a bearing. Consistency measurements are therefore of little assistance in the selection of greases.

The other test which must be used with a knowledge of its limitations is the drop-point determination. A minimum drop-point requirement is a simple means of eliminating obviously unsuitable products, but the fact that a grease has a drop-point above the minimum requirement does not mean that the lubricant will be satisfactory even at temperatures well below its drop-point.

The Sub-Committee responsible for standardizing the drop-point test have stated that it should not necessarily be considered as having any bearing on service performance.

There is therefore a need for standard methods which can be used for the selection of greases for various purposes.

Such methods could be classified as tests for greases suitable for use at (*a*) low speeds and moderate temperatures and (*b*) high speeds and high

* Acknowledgments are due to Mr. H. S. Wood and Mr. R. H. Unsworth for assistance in the experimental work on which this paper is based.

temperatures. Into category (*a*) would fall general purpose greases of the lime-base type, and category (*b*) would include greases of the soda-base type.

The methods of test should simulate practical conditions as far as possible. In the same way that the standard method for fuel testing uses an actual engine for the determination of octane number, so a standard method for testing greases should employ a bearing, unless the properties can be precisely defined by the results of fundamental measurements.

The requirements for a desirable grease are: (1) the ability to lubricate a bearing for long periods at all temperatures and speeds at which the equipment is to be operated; (2) complete stability and retention of properties on storage, both in its container and in a bearing; (3) capability of being dispensed by normal grease guns and lubricators.

In order to lubricate a bearing, the grease must remain in the place where it is most required. The surfaces of a ball bearing which require lubrication are those of the balls and tracks. Grease which remains in any other position in the bearing does no useful work unless it acts as a reservoir for the replenishment of the tracks.

Normal lime-base greases, if used at temperatures below 50° C. and in bearings of low periphery speeds, tend to maintain lubrication by flowing into the tracks. A moderate rate of shear is sufficient to cause such greases to attain some degree of fluidity. High rates of shear tend to reduce the apparent viscosity to a value which is relatively close to that of the base oil, and the lubricant is soon lost in a high-speed bearing. This can be illustrated by the apparent viscosities of a lime-base grease which were found to be 80 poises at a rate of shear of 15 secs.$^{-1}$ and 3·3 poises at a rate of shear of 10,000 secs.$^{-1}$ The viscosity of the base oil was 2·1 poises.

It is obvious that some form of viscometric measurement will provide useful information on lime-base greases. A pressure viscometer which has been developed in the U.S.A. is probably one of the most convenient instruments for such measurements. It consists of a cylinder fitted with a capillary orifice through which the grease is forced by a piston operated hydraulically at a known pressure. By measuring the pressure required to cause the grease to flow at a given rate and knowing the dimensions of the capillary the apparent viscosity can be calculated.

Since the cohesion and adhesion of most lime-base greases are similar, the product which will be retained in the bearing to the greatest extent can be selected by flow measurements without tests in a bearing.

Unfortunately, lime-base greases which depend on water for their structure are very prone to be unstable in use and in storage. Despite the number of heat tests which have been proposed for measuring stability, it cannot yet be stated that a satisfactory solution has been found.

Two types of instability occur in service. In one case either a sticky resinous substance or a hard varnish is formed in the bearing. This type of failure is undoubtedly due to the oxidation and polymerisation of unsaturated constituents. It is usually found that greases of this nature absorb oxygen in a bomb fairly rapidly at 100° C. and become fluid, whilst greases not prone to this type of failure absorb oxygen slowly and retain their consistency.

A rapid method of eliminating oxidizable greases consists of heating a

film of the grease in a bearing at a temperature of 120–150° C. and measuring the torque required to turn the cooled bearing through the first revolution after a definite period of heating.

The other type of failure arises from greases which on testing by normal heat tests appear to be stable, and in fact are stable when stored in bulk.

When applied to a bearing, capillary forces appear to extract the oil from the soap and leave a white deposit under the balls of the bearing. The failure is often associated with excess of alkali which tends to precipitate the soap.

It has been found that if a bearing packed with such a grease is placed on an absorbent pad and heated for about a week at a temperature about 10° C. below the drop-point, the grease becomes of a cheese-like nature and the bearing is no longer free turning.

The author has met two extreme cases of failure of the above types. In the first case the grease was slightly acid and all-steel bearings filled with the grease were found to seize completely in six weeks.

In heat tests at 130° C. the grease failed to re-set on cooling, and it was thought that such a test would provide an adequate safeguard against seizure of bearings. Samples of grease were obtained which solidified after heating and suffered little loss of oil when heated and inverted in the dish at room temperature for a week. Bearings were packed with the greases and stored in grease-proof paper in cardboard boxes at 40° C. When the bearings were inspected after three weeks, the bearing packed with the grease which was thought to be the most stable had seized completely, and a white deposit was found under each ball.

After a number of tests, it was found that only tests involving capillary action would eliminate greases of this type.

The methods for testing lime-base greases should therefore include (1) flow measurements at various rates of shear and various temperatures, (2) an oxidation test with an examination of the oxidation product, and (3) a syneresis test involving capillary action.

Other types of grease, such as soda base and lithia base, vary widely in their texture, cohesion, and adhesion, and it is on such properties that the lubrication of a high speed bearing depends.

It is with high speed and high-temperature lubricants that the need for practical testing is clearly indicated.

If a grease has no adhesion to metal little lubrication is possible; whilst if it possesses good adhesion but little cohesion, high-speed rotation will cause the bulk of the grease to break away from the film adhering to the balls and there will be no reservoir of lubricant available for the replenishment of the tracks. If both adhesion and cohesion are moderately high a strong link is set up between the film on the balls and the bulk of the grease and a continual circulation of lubricant takes place.

The question now arises as to how the combined cohesion and adhesion properties are to be measured.

It is well known that a lightly loaded bearing which contains no grease exerts little torque on the housing when it rotates, but if grease is applied a high torque is exerted during the first rotation. The magnitude of this torque depends to a large extent on the consistency of the grease. During subsequent rotations, if the grease channels, due to a low cohesion, the

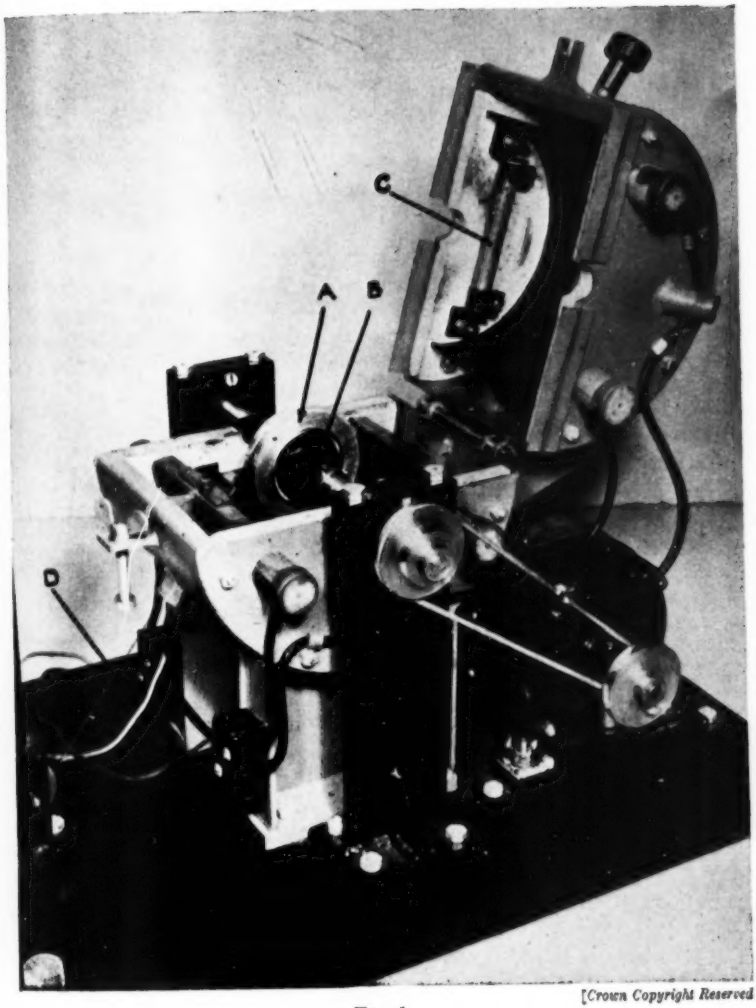

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FIG. 1.

[To face p. 250.]

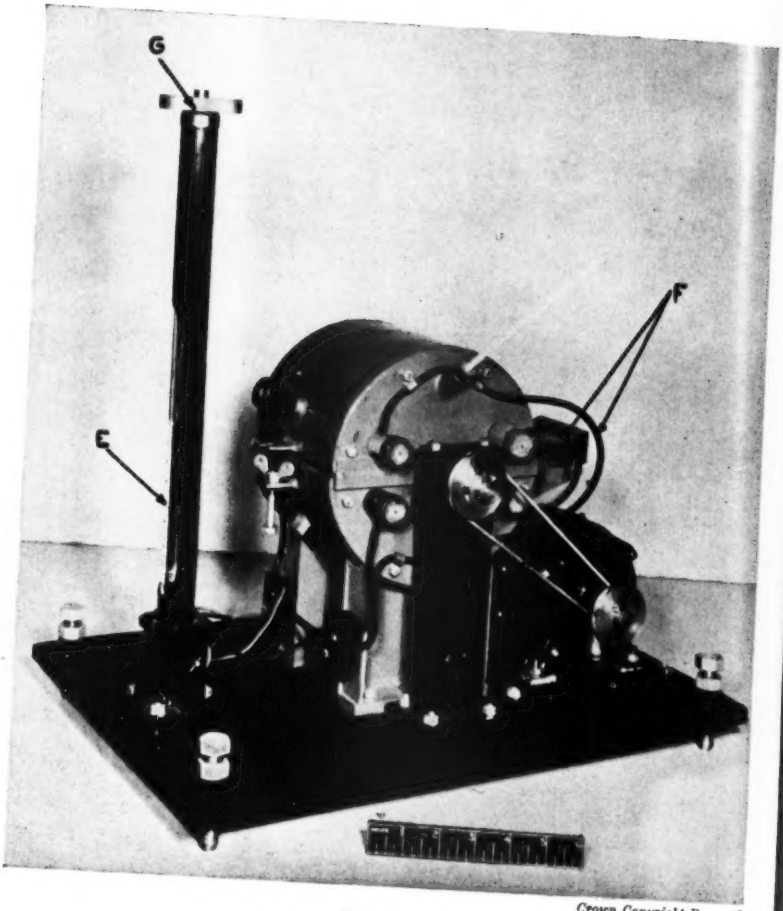

FIG. 2.

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torque will fall rapidly; on the other hand, if the grease replenishes the tracks the torque will remain high and any fall will be due to a breakdown of the structure under shearing forces.

Torque measurements therefore provide a means of studying the combined effects of cohesion and adhesion.

A suitable apparatus is shown in the accompanying photographs (Figs. 1 and 2). It consists of a B.R.L.020 bearing, *B*, mounted in a drum, *A*, on a rotatable shaft. The torque transmitted to the drum is measured by means of a thread, *D*, connected to a calibrated spring torque meter, *E*.

In use, the bearing is filled with a known weight of grease by forcing it in from one side. The bearing is mounted in the drum and on the shaft in an electrically heated box. The box is heated to a temperature of 37·8° C. (100° F.), and maintained at this temperature for 2 hours. At the end of the first hour the shaft is rotated at a speed of 600 r.p.m. and readings of torque taken after 15 seconds, 5 minutes, and 60 minutes. The bearing is cooled, wiped on the outside, and re-weighed for the determination of grease loss.

The bearing is remounted in the apparatus and the temperature raised to a value slightly higher than that to which the grease is to be subjected in service. This temperature is maintained for 2 hours. At the end of the first hour the shaft is rotated at a speed approximating to that operating in the equipment to be lubricated. Torque readings are not taken during this rotation.

In order to ascertain the changes that have been produced at the higher temperature, the grease is cooled to 100° F. (37·8° C.), and torque readings are taken as before. The bearing is re-weighed for the determination of the total grease loss.

If the two sets of torque readings are of a similar order it is clear that the grease has remained in the tracks and that little change in cohesion and adhesion has taken place.

The repeatability of the test is good provided that the bearings used are in an unworn condition.

The following results were obtained on a grease when using three different new bearings selected at random from a batch of a dozen. The torque readings were taken at 37·8° C. and 600 r.p.m. both before and after rotation at 176° C. and 2500 r.p.m.

(*a*) Initial run.
(*b*) After high temperature run.

Bearing.	Torque, gm. cm.			Grease Losses.	
	15 seconds.	5 minutes.	60 minutes.	Run (*a*), %.	Run (*b*), %.
1 (*a*)	1067	640·5	427	40·3	—
(*b*)	1037	701·5	427	—	74·2
2 (*a*)	1037	610	457·5	37·9	—
(*b*)	1006	701·5	427	—	72·4
3 (*a*)	1098	610	457	37·9	—
(*b*)	1067	640	442	—	72·4

In Fig. 3 the results of tests on a number of greases have been plotted to show how the test differentiates between channelling and non-channelling greases.

The selection of the most suitable torque limits must be influenced by the knowledge that if the cohesion is too high an abnormal temperature rise will occur in service, owing to the work which has to be done in overcoming the cohesion. For the particular bearing used a value of 300–700 gm. cm. after 5 minutes is probably satisfactory, since greases having this torque value have given good performances in service.

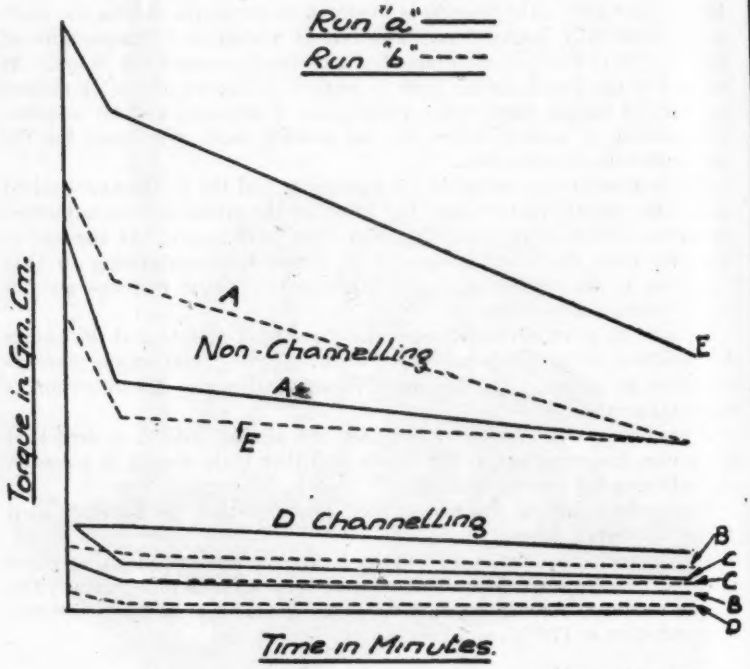

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FIG. 3.

CLASSIFICATION OF GREASES INTO CHANNELLING AND NON-CHANNELLING TYPES BY TORQUE TESTS.

The other criterion of performance which must be considered when examining the results of the test, is that of rate of change of torque with time. A change of 50 per cent. from the 15 seconds value to the 5-minute value is not excessive, but the fall from the 5-minute figure to the final torque should not be more than 40 per cent. The changes produced by the higher temperature rotation should be as small as possible. Values between 70 and 150 per cent. are not excessive. The above tests are probably adequate for most purposes, but it is advisable to supplement them by a test of longer duration.

A method which gives valuable information consists of churning one half pound of the grease, by rotating a bearing in it, at a temperature about 20° C. below its drop-point. The bearing should be run at high speed, and the test may be conveniently run for 7 hours. The grease is then cooled and inspected for liquefaction, oil separation, and granulation. The sample is then subjected to the torque tests previously described.

The results obtained by such a test are illustrated by the data obtained on the grease used in the repeatability tests mentioned earlier.

Run.	Torque, gm. cm.			Grease Losses.	
	15 seconds.	5 minutes.	60 minutes.	Run (*a*), %.	Run (*b*), %.
(*a*) . .	1174	823	549	53·3	—
(*b*) . .	1067	732	488	—	80·6

It is obvious that the grease has retained its basic structure and that its cohesion and adhesion have undergone little change.

For most greases the above tests should reveal any tendency towards instability, but one exception has been found. One grease, which behaved well in the torque tests, when heated in the presence of a copper strip showed a marked degree of liquefaction. This shows the difficulty of devising a test which is of universal application.

The test methods outlined above cover the basic properties of most greases, but other tests are necessary if the grease is to operate under special conditions, such as in the presence of water or at low temperature. Water, by emulsifying with or dissolving constituents of the grease, may radically change the cohesion and adhesion, whilst high cohesion and adhesion will be undesirable at low temperatures.

The fact that a grease has sufficient cohesion and adhesion to give a reasonable performance in the high-speed tests does not mean that the grease will cause undue trouble in starting the equipment at low ground temperatures.

The following values of the product of torque and time for the first revolution produced by this torque were obtained on the grease which has been used as an example earlier in this paper.

Temperature, °C.	Product of Torque and Time, gm. cm. secs.
25	320·25
20	457·5
15	732
10	1,098
0	2,074
− 5	4,727
−10	7,808
−15	10,705

The bearing is reasonably free turning if the torque–time product does not exceed a value of 20,000, so that the grease will allow an easy start at temperatures down to at least − 15° C.

It is of interest to note that if the above results are plotted on a semi-log. scale, the points lie fairly close to a straight line.

Summarizing, the methods for testing which are advocated are as follows :—

(*a*) Flow measurements at different rates of shear and at various temperatures.
(*b*) Oxidation tests with an examination of the oxidized product.
(*c*) Bleeding tests involving capillary action.
(*d*) Torque tests at two speeds and temperatures.
(*e*) Churning test at high speed and temperature.
(*f*) Special tests for particular applications which involve conditions likely to modify the properties of the grease on which its performance in the above tests depends.

A RATIONAL BASIS FOR THE VISCOSITY INDEX SYSTEM. PART I.

E. W. Hardiman, B.Sc., M.Inst.Pet., and Alfred H. Nissan, D.Sc., M.Inst.Pet.

Introduction.

The necessity for providing a satisfactory method of comparing the viscosity–temperature characteristics, or change of viscosity with temperature, of oils has long been recognized, particularly in the field of automotive and aviation lubricants, and has resulted in the presentation of a large number of suggested methods whereby this property of an oil could be expressed. Chief among these are the Viscosity Index system, the viscosity pole height, and the so-called A.S.T.M. slope. The Viscosity Index system,[1] which has been adopted by the Institute of Petroleum and American Society for Testing Materials Committee D-2, is based on a comparison of the viscosity of the oil under test at 100° F. and 210° F., with two sets of reference oil viscosity figures representing upper and lower extremes in viscosity–temperature susceptibility. Viscosity pole height,[2] which has been in use in Germany for several years, was based on the assumption, now found to be only partly true, that when viscosity–temperature relationships are plotted on a suitable scale to give a straight line, such straight lines for oils of the same origin or chemical type will meet at a common point known as the viscosity "pole." The distance of this "pole" from the base line is known as the "pole height," and for ordinary mineral lubricating oils this value ranges from 1·0 to 6·0, increasing values representing increasing steepness in the viscosity–temperature curve. A.S.T.M. slope characterizes an oil in terms of the angle of the straight viscosity–temperature line obtained by plotting viscosity–temperature data on the A.S.T.M. Chart for liquid petroleum products, D 341–39.[3] This last system has lately increased in popularity in America, being used particularly for those oils having good viscosity–temperature characteristics, *i.e.*, showing flat viscosity–temperature curves, such as aviation hydraulic oils, for which other methods are, at present, less suitable. These three systems all have certain disadvantages and anomalies as a result of which no one of them has been universally adopted, although the Viscosity Index system is by far the most widely used of the three.

The purpose of the work described in this paper was to make a careful examination of the system most widely in use—namely, the Viscosity Index system, and endeavour to eradicate those disadvantages and anomalies which present limitations to its usefulness and universal acceptance; in so doing an attempt was made to derive a mathematical basis for the Viscosity Index system. In view, however, of the very large background of testing and research built up using the Viscosity Index system, which has now been in use for some fifteen years, it was considered that any modifications which might be found necessary should be such as to interfere as little as possible with the present system between the V.I. values of 0 and 100.

Viscosity Index.

The viscosity index of an oil, as propounded by E. W. Dean and G. H. B. Davis in 1929,[4] was an expression of its viscosity–temperature characteristics in terms of its Saybolt viscosities at 100° F. and 210° F. In effect, it was a comparison of the viscosity at 100° F. of the oil under test with those of two reference oils representing, respectively, 0 and 100 on the V.I. scale, each having the same viscosity at 210° F. as the oil under test. The basic data used in developing the system were obtained from Saybolt viscosity determinations at 100° F. and 210° F. on two series of lubricating-oil fractions, designated the L series and the H series, and derived, respectively, from two crudes chosen at the time as exhibiting the greatest and the smallest change of viscosity with temperature. The H series of oils, derived from a Pennsylvanian crude, was arbitrarily assigned the viscosity index value of 100, and the value of 0 was given to the L series. By plotting viscosity data at 100° F. against those values obtained at 210° F., curves were obtained for both the L series and the H series which were extrapolated upwards to 160 Saybolt seconds at 210° F., the lower limit being fixed at 40 seconds at 210° F., as representing the lowest practical viscosity determination obtainable with the Saybolt instrument.

The viscosity index of a given oil was then calculated from the equation:—

$$\text{V.I.} = \frac{L - U}{L - H} \times 100 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where U = Viscosity (S.U.) at 100° F. of the oil under test.

L and H = Viscosities (S.U.) at 100° F. of the series L and H oils respectively, having the same viscosity at 210° F. as the oil under test.

In 1932 revised basic data for the L and H series were published by Davis, Lapeyrouse, and Dean [4] for the viscosity range between 50 seconds and 40 seconds at 210° F., since it had been found that the original data did not yield consistent results, probably due to the limitations in the accuracy of the Saybolt viscometer for efflux times of less than 50 seconds. At a later date the need became apparent for extension into the viscosity region below 40 seconds (S.U.) at 210° F., and again because of the limitations of the Saybolt viscometer, a new basic V.I. table was presented by Dean, Bauer, and Berglund in 1940,[5] based on kinematic viscosities in centistokes instead of Saybolt seconds in which the lower viscosity limit was placed at 2·0 cs. at 210° F. and the upper limit extended to 75·0 cs. at 210° F. This change in viscosity units was particularly opportune in view of the rapidly increasing use of the glass-type kinematic viscometers for oil testing. The extension down to 2·0 cs. was of an empirical nature, and it was found necessary to make some slight adjustments in the range already revised by Davis, Lapeyrouse, and Dean in order to preserve a degree of uniformity in the curves. These revised data form the basis of the Viscosity Index system as used to-day.

Limitations of the Viscosity Index System.

Although the Viscosity Index system as briefly described has met with a very wide degree of acceptance in many countries, it has become apparent that in its present form its limit of usefulness has been reached, and future lubricating oil requirements are likely to call either for a new method of expressing viscosity–temperature characteristics or for some degree of modification to the present system.

The chief reason why these changes are necessary arises from the need for assigning viscosity indices to oils having better viscosity–temperature characteristics than those represented by 100 on the V.I. scale—*i.e.*, better than the original Pennsylvanian oils used by Dean and Davis for their work. Improvements in methods of refining lubricating oils and the increased use of viscosity index improvers have resulted in the production of oils having viscosity indices up to 140, or even higher. Although equation (1) permits a viscosity index higher than 100 to be determined for a given oil, these values over 100 are, from the nature of the equation, comparatively meaningless, as can be well illustrated in a curve relating kinematic viscosity at 100° F. with kinematic viscosity at 210° F. for sets of oils of different viscosity indices. Fig. 1 shows that as the viscosity index increases from 0, the curvature of the viscosity relationship decreases until at some point between 120 and 130 a straight line is obtained. At still higher viscosity index values the curvature is reversed until at 150 V.I. the anomaly is demonstrated that two oils having the same viscosity at 100° F., but different viscosities at 210° F., would both have the same V.I. of 150. For example, two oils, both having viscosities of 80·0 cs. at 100° F., but viscosities of 15·5 cs. and 41·5 cs. at 210° F., are each assigned the same viscosity index of 150. This failure becomes even more marked with increasing V.I. With oils having comparatively high viscosities at 210° F., the anomaly becomes apparent much lower down the V.I. scale, and, generally speaking, it could be stated that the Viscosity Index system breaks down at 130 V.I. This particular feature of the Viscosity Index system is generally realized, and Larson and Schwaderer, for example, directed attention to it in their paper on "Viscosimetry and New Graphical Viscosity Classifications." [6]

A second disadvantage to the present system, though not perhaps of such a serious nature as the first, is that V.I. is based on two fixed temperatures, 100° F. and 210° F. Apart from the inconvenience and the possibility of error introduced by the need for extrapolating back to these two temperatures in those cases where other temperatures are more commonly specified or used for viscosity determinations, the fixing of 100° F. and 210° F. as basic temperatures imposes a limit to the type of product to which viscosity index can be applied, and those products, such as diesel oils, kerosines, and gasolines, which have viscosities lower than 2·0 cs. at 210° F. cannot be included in the system. It is suggested that the possibility of applying viscosity index to such products would be of considerable interest, and might increase our knowledge regarding the inter-relation between composition and behaviour, and would provide a convenient method whereby products of different composition and origin could be distinguished. Such an extension in the application of viscosity index

would be obtained if an equation were derived by means of which V.I. could be obtained from viscosity data at any two temperatures.

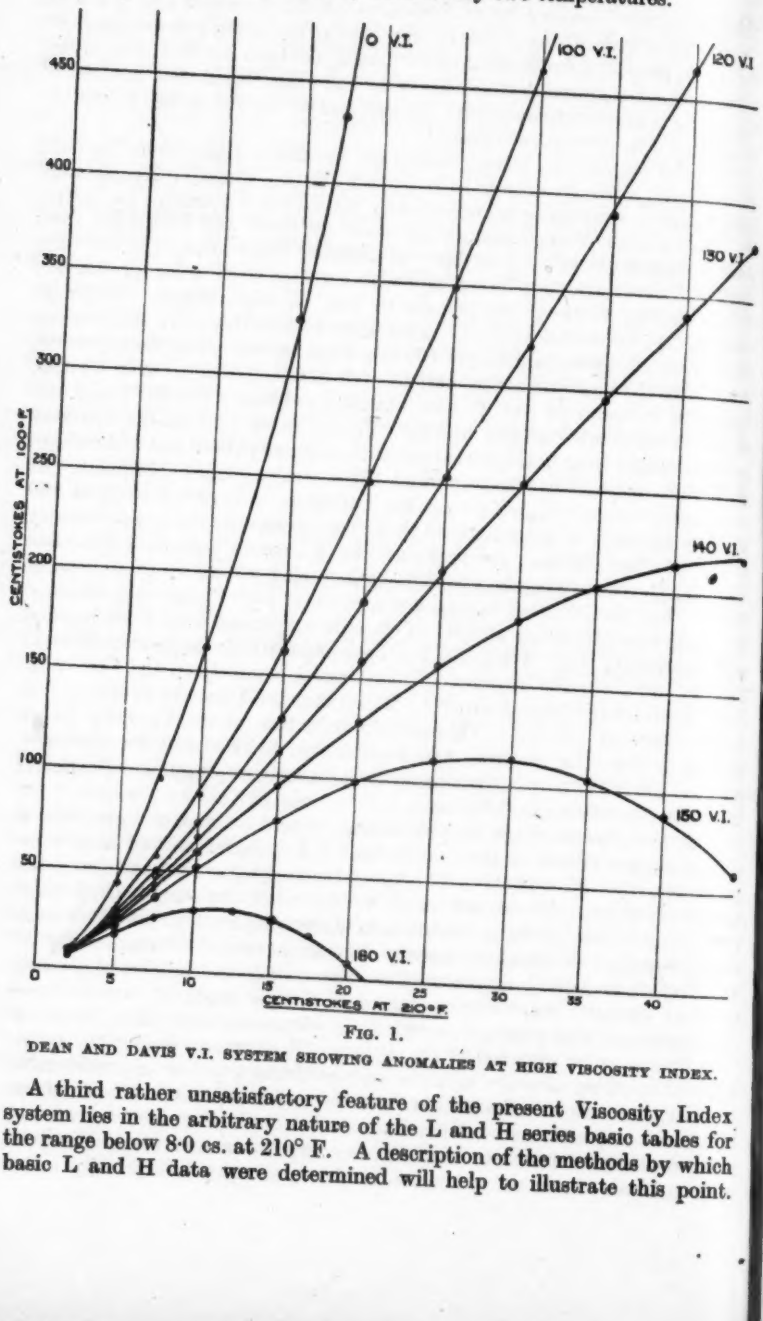

FIG. 1.

DEAN AND DAVIS V.I. SYSTEM SHOWING ANOMALIES AT HIGH VISCOSITY INDEX.

A third rather unsatisfactory feature of the present Viscosity Index system lies in the arbitrary nature of the L and H series basic tables for the range below 8·0 cs. at 210° F. A description of the methods by which basic L and H data were determined will help to illustrate this point.

The L and H series above 8·0 cs. at 210° F. are still based on the original experimental work carried out by Dean and Davis, from which the following two equations were derived :—

$$\text{Series H}: y = 0{\cdot}0408x^2 + 12{\cdot}568x - 475{\cdot}4 \quad . \quad . \quad . \quad (2)$$

$$\text{Series L}: y = 0{\cdot}216x^2 + 12{\cdot}07x - 721{\cdot}2 \quad . \quad . \quad . \quad . \quad (3)$$

where y = Saybolt viscosity at 100° F.
x = Saybolt viscosity at 210° F.

Viscosities calculated by the above equations, compared with experimentally determined figures from the original paper by Dean and Davis [1] showed that for the H series over the range studied, from 49·0 to 105·0 Saybolt seconds at 210° F. (corresponding approximately to 7·0–21·6 cs. at 210° F.) the equation (2) fitted the experimental data to within 1·0 per cent.

In the L series a somewhat narrower range of viscosities at 210° F. was studied, 42·0–71·0 Saybolt seconds (corresponding to a range of 4·8–13·2 cs. at 210° F.), while data calculated from equation (3) showed a maximum deviation from the experimental values of about 5 per cent. Although, from the nature of the V.I. scale, the accuracy of the H series is of greater importance than the L series, it would appear that the eventual extrapolation of the H series back to 75·0 cs. at 210° F. was more justifiable than the L series.

As has already been mentioned, Davis, Lapeyrouse, and Dean published in 1932 a revised data table for the L and H series between 40 and 50 Saybolt seconds at 210° F. to rectify certain inconsistencies which were found in the original data,[4] but these revised tables were purely empirical. In 1940, Dean, Bauer, and Berglund [5] extended the V.I. system down to 2·0 cs. at 210° F., again empirically, so that the final complete tables as published in 1940 actually consist of three separate groups of data which could be represented by three distinct curves having different equations. These three curves themselves form one continuous complex curve.

Fenske and co-workers [7] expressed disagreement with the earlier basic data tables, and published alternative viscosity data for the L and H series, based on kinematic viscosity determinations on cuts fractionated from Pennsylvanian crudes, not, of course, necessarily representative of the crudes used by Dean and Davis for their original work. These tables, published by Hersh, Fisher, and Fenske, do not agree with the latest tables by Dean, Bauer, and Berglund, and would, in fact, assign higher viscosity indices than 100 to the oils in the lower viscosity range represented by the viscosity data in the 1940 tables. It will be seen, therefore, that while the data above 8·0 cs. at 210° F. can be taken as satisfactory for the H series, and reasonably satisfactory for the L series, there is reason to doubt the authenticity of the data below 8·0 cs. The reason for this lack of agreement can probably be found in the basis of the V.I. scale that all lubricating fractions from the Pennsylvanian and Texas crudes would have the same viscosity–temperature characteristics. Experience has shown that this assumption is not necessarily correct, and in many cases light lubricating-oil fractions from a given crude exhibit considerably better viscosity–temperature characteristics than the higher viscosity fractions from the same crude.

Present Work.

The present work was undertaken with a view to eliminating from the V.I. system the three disadvantages already described, thereby enabling viscosity index to be applied to oils of very widely varying viscosity-temperature characteristics, so that even the so-called "perfect" oil, exhibiting no change of viscosity with temperature, could as readily be included in the system as the more normal oils. Secondly, it was hoped to make the system applicable to any two temperatures, instead of the two fixed temperatures 100° F. and 210° F. at present in use, and thirdly it was desired to define the lower viscosity values in the L and H series on some more fundamental basis.

Since an effort was being made to provide a theoretical background to the V.I. system, the fundamental equation relating viscosity with temperature for a given oil was taken as the starting point. This relationship can be summarized by a simple exponential formula of the type :—

$$\mu = A_1 e^{\frac{B}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where μ = absolute viscosity,
T = absolute temperature,
A_1 and B = constants

(in practice, it is found that A_1 and B are not quite constant, but vary with temperature).

The validity of the equation is not seriously affected if, instead of μ we substitute ν, or kinematic viscosity, and taking into account the temperature effect on A_1, the following equation becomes applicable :—

$$\nu = AT^{\frac{1}{2}} e^{\frac{B}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

since it is known that A_1 is a function of $T^{\frac{1}{2}}$. Thus A in equation (5) can be taken as very nearly constant with temperature. From equation (5) we can state that :—

$$v_1 = v_2 \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}} e^{\frac{B(T_2 - T_1)}{T_2 T_1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where v_1 and v_1 are kinematic viscosities at temperature T_1 and T_2 respectively.

If the temperature range is fixed, then all functions involving T_1 and T_2 alone become constants, and we arrive at the relationship :—

$$v_1 = k \, . \, v_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In this equation, however, we are still making the incorrect assumption that B is a constant, and a more appropriate equation, therefore, would be :—

$$v_1 = kf(v_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where k = constant for a fixed temperature range, but varies with temperature range.

Equation (8) is the equation to a straight line obtained by plotting v_1 against some function of v_2, and k will be the tangent of the angle subtended by this straight line and the axis.

TABLE I.

Data used as Basis for Experimental Work.

Vis. at 210° F.	Viscosity at 100° F. for Viscosity Index of—								
	0.	10.	25.	40.	50.	60.	75.	90.	100.
8·0	108·9	104·3	97·6	90·8	86·3	81·8	75·0	68·2	63·7
9·0	135·2	129·3	120·5	111·6	105·8	99·9	91·1	82·2	76·4
10·0	162·5	155·2	144·2	133·2	125·8	118·5	107·5	96·5	89·2
12·0	223·1	212·5	196·5	180·5	169·8	159·2	143·2	127·2	116·5
14·0	292·4	277·8	255·9	234·0	219·4	204·8	182·9	161·0	146·4
16·0	369·1	350·0	321·4	292·7	273·6	254·5	225·9	197·3	178·2
18·0	455·7	431·4	395·0	358·5	334·2	309·9	273·5	237·0	212·7
20·0	551·1	520·9	475·6	430·4	400·2	370·0	324·8	279·5	249·3
22·0	654·9	618·2	563·2	508·1	471·4	434·7	379·7	324·6	287·9
24·0	768·0	724·1	658·2	592·3	548·3	504·4	438·5	372·6	328·6
26·0	889·6	837·8	760·0	682·2	630·4	578·6	500·8	423·0	371·2
28·0	1018	958	868	777	717	656	566	475	415
30·0	1156	1086	982	878	808	739	635	530	461
35·0	1535	1440	1297	1154	1059	964	821	678	582
40·0	1967	1842	1654	1466	1341	1216	1028	840	715

Taken from Standard Oil Development Co.'s Circular 30.53, March 1939.

The data on which the present work was based are shown in Table I, and were taken from the Standard Oil Development Co.'s Circular No. 30.53, of March 1939, and represent the data obtained by Dean, Bauer, and Berglund as published in 1940. It will be seen that the data have been limited to the range 8·0–40·0 cs. at 210° F. for the reasons already stated.

Taking equation (8) as a basis, experimental plotting showed that the function of v_2 which enabled straight-line relationships to be obtained was v_2^n, where n varied according to the type of oil. Thus for 100 V.I. oils it was found that when $n = 1{\cdot}51$ a straight-line relationship was obtained, where k was equal to 2·714. According to the equation, k is a constant for the two fixed temperatures, and should therefore have the same value irrespective of V.I., and this was substantiated, since with the 0 V.I. data a straight line was obtained when $n = 1{\cdot}78$, and k was again equal to 2·714. These curves are illustrated in Fig. 2, from which it will be noted that the accuracy of this relationship is sufficiently close to justify using it as a basis for the work. This procedure was repeated for viscosity curves representing 10, 25, 40, 50, 60, 75, and 90 V.I. oils, and in each case, when the value of n was determined, which gave the nearest approach to a straight line, the value of k was 2·714. Equation (8) can therefore be amplified into :—

$$v_1 = k \cdot v_2^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

k = function of temperature range alone and is independent of the nature of the oil,

n = characteristic constant of the oil, and is also a function of temperature range.

It was found experimentally that this relationship holds for other temperature ranges, and in each case n appeared to be a constant charac-

teristic of the oil multiplied by a function of the temperature range, while k appeared to vary with temperature range only. Thus, if the nature of the variation of n and k were accurately ascertained, an equation would

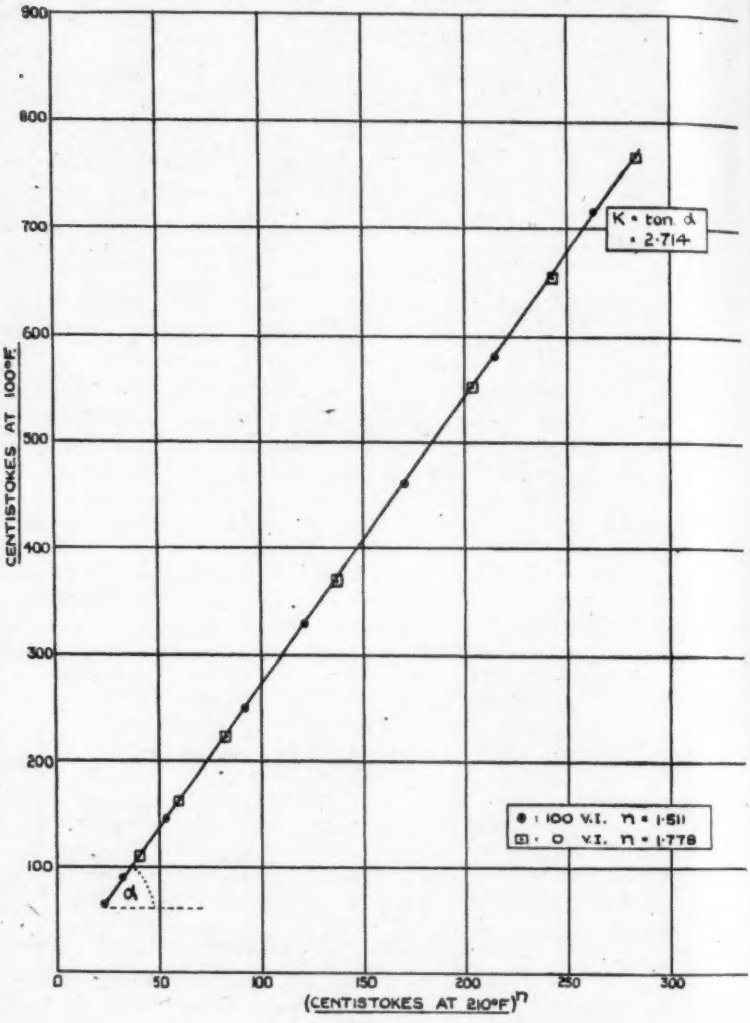

FIG. 2.

V_{100} PLOTTED AGAINST V_{210}^{n}.

be arrived at whereby the characteristic constant of an oil could be determined from viscosity data obtained at any two temperatures. This particular aspect of the investigation has involved a considerable amount of work, and will be discussed separately in a later paper.

Since k is known for the temperature range 100–210° F., equation (9) can now be rewritten in the following form :—

$$n = \frac{\log v_1 - 0{\cdot}4336}{\log v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

(since $\log k = 0{\cdot}4336$).

The Relation Between "n" and V.I.

Since it has been stated that "n" is the characteristic constant of a given oil, it appeared that there must be some relationship between n and viscosity index, and Fig. 3 shows that when the two constants are

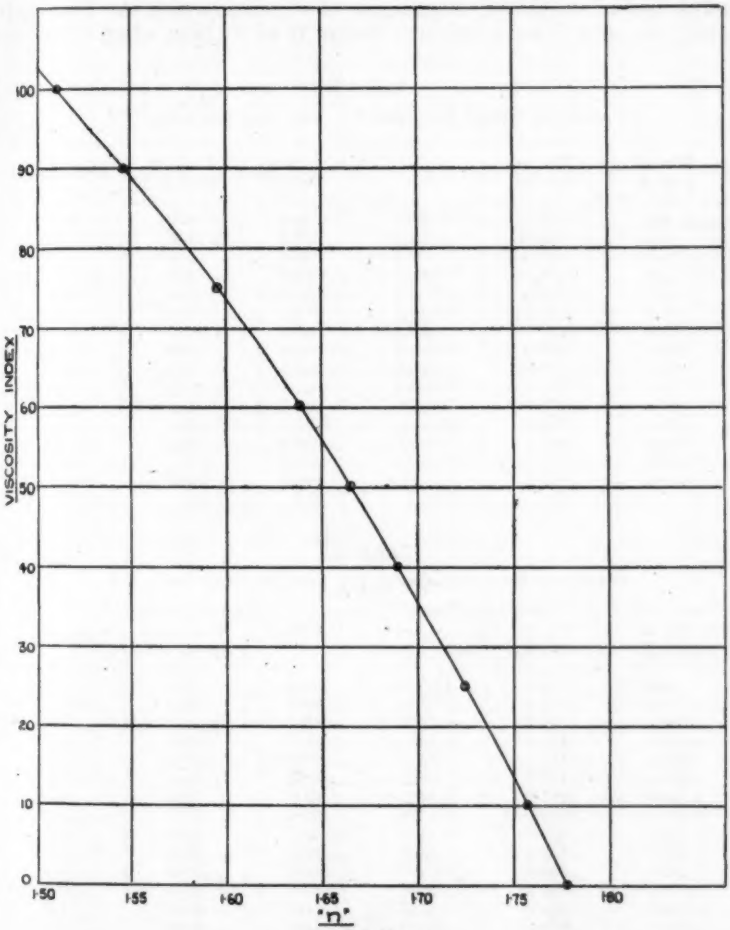

Fig. 3.

SHOWING RELATION BETWEEN "n" AND V.I.

plotted, a smooth curve is obtained. From this curve it was found that when V.I. was plotted against antilog n a straight line was obtained, and the following empirical equation was found by which n could be converted directly into V.I.:—

$$\text{V.I.} = (60{\cdot}0 - \text{antilog } n) \times 3{\cdot}63 \quad . \quad . \quad . \quad . \quad (11)$$

Practical Application.

The use of equations (10) and (11) enables viscosity index to be calculated directly from the vscosity determinations of a given oil at 100° F. and 210° F. without the necessity for any comparison with the L and H series basic data tables. The degree of correlation with the Dean and Davis viscosity index is shown in Tables II to X, from which it will be

Table II.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean & Davis V.I.	Difference.
8·0	63·7	1·5175	98·3	100	−1·7
9·0	76·4	1·5191	97·8	100	−2·2
10·0	89·2	1·5168	98·5	100	−1·5
12·0	116·5	1·5131	99·5	100	−0·5
14·0	146·4	1·5113	100·0	100	Nil
16·0	178·2	1·5094	100·5	100	+0·5
18·0	212·7	1·5089	100·6	100	+0·6
20·0	249·3	1·5089	100·6	100	+0·6
22·0	287·9	1·5091	100·6	100	+0·6
24·0	328·6	1·5095	100·5	100	+0·5
26·0	371·2	1·5095	100·5	100	+0·5
28·0	415·0	1·5094	100·5	100	+0·5
30·0	461·0	1·5097	100·4	100	+0·4
35·0	582·0	1·5098	100·3	100	+0·3
40·0	715·0	1·5109	100·0	100	Nil

Table III.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and David V.I.	Difference.
8·0	68·2	1·5504	88·9	90·0	−1·1
9·0	82·2	1·5524	88·3	90·0	−1·7
10·0	96·5	1·5509	88·7	90·0	−1·3
12·0	127·2	1·5483	89·5	90·0	−0·5
14·0	161·0	1·5471	89·8	90·0	−0·2
16·0	197·3	1·5460	90·2	90·0	+0·2
18·0	237·0	1·5462	90·0	90·0	Nil
20·0	279·5	1·5471	89·8	90·0	−0·2
22·0	324·6	1·5477	89·7	90·0	−0·3
24·0	372·6	1·5487	89·4	90·0	−0·6
26·0	423·0	1·5496	89·1	90·0	−0·9
28·0	475·0	1·5496	89·1	90·0	−0·9
30·0	530·0	1·5508	88·7	90·0	−1·3
35·0	678·0	1·5527	88·2	90·0	−1·8
40·0	840	1·5546	87·6	90·0	−2·4

TABLE IV.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Difference.
8·0	75·0	1·5961	74·5	75·0	−0·5
9·0	91·1	1·5991	73·5	75·0	−1·5
10·0	107·5	1·5978	74·0	75·0	−1·0
12·0	143·2	1·5959	74·5	75·0	−0·5
14·0	182·9	1·5955	74·8	75·0	−0·2
16·0	225·9	1·5948	75·0	75·0	Nil
18·0	273·5	1·5959	74·5	75·0	−0·5
20·0	324·8	1·5972	74·2	75·0	−0·8
22·0	379·7	1·5984	73·8	75·0	−1·2
24·0	438·5	1·6000	73·3	75·0	−1·7
26·0	500·8	1·6015	72·8	75·0	−2·2
28·0	566·0	1·6027	72·4	75·0	−2·6
30·0	635·0	1·6039	72·0	75·0	−3·0
35·0	821·0	1·6065	71·1	75·0	−3·9
40·0	1028·0	1·6094	70·2	75·0	−4·8

TABLE V.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Difference.
8·0	81·8	1·6379	60·1	60·0	+0·1
9·0	99·9	1·6412	58·9	60·0	−1·1
10·0	118·5	1·6402	59·3	60·0	−0·7
12·0	159·2	1·6385	59·9	60·0	−0·1
14·0	204·8	1·6383	60·0	60·0	Nil
16·0	254·5	1·6378	60·1	60·0	+0·1
18·0	309·9	1·6392	59·6	60·0	−0·4
20·0	370·0	1·6407	59·1	60·0	−0·9
22·0	434·7	1·6423	58·5	60·0	−1·5
24·0	504·4	1·6440	57·9	60·0	−2·1
26·0	578·6	1·6458	57·2	60·0	−2·8
28·0	656·0	1·6468	56·8	60·0	−3·2
30·0	739·0	1·6485	56·2	60·0	−3·8
35·0	964·0	1·6517	55·0	60·0	−5·0
40·0	1216·0	1·6548	53·9	60·0	−6·1

TABLE VI.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Difference.
8·0	86·3	1·6636	50·5	50·0	+0·5
9·0	105·8	1·6671	49·3	50·0	−0·7
10·0	125·8	1·6661	49·6	50·0	−0·4
12·0	169·8	1·6646	50·0	50·0	Nil
14·0	219·4	1·6644	50·1	50·0	+0·1
16·0	273·6	1·6639	50·4	50·0	+0·4
18·0	334·2	1·6653	49·8	50·0	−0·2
20·0	400·2	1·6669	49·2	50·0	−0·8
22·0	471·4	1·6685	48·6	50·0	−1·4
24·0	548·3	1·6703	47·9	50·0	−2·1
26·0	630·4	1·6721	47·2	50·0	−2·8
28·0	717·0	1·6735	46·6	50·0	−3·4
30·0	808·0	1·6748	46·1	50·0	−3·9
35·0	1059·0	1·6782	44·8	50·0	−5·2
40·0	1341·0	1·6814	43·6	50·0	−6·4

TABLE VII.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Differences.
8·0	90·8	1·6881	40·8	40·0	+0·8
9·0	111·6	1·6916	39·4	40·0	−0·6
10·0	133·2	1·6910	39·6	40·0	−0·4
12·0	180·5	1·6891	40·4	40·0	+0·4
14·0	234·0	1·6888	40·5	40·0	+0·5
16·0	292·7	1·6882	40·8	40·0	+0·8
18·0	358·5	1·6895	40·2	40·0	+0·2
20·0	430·4	1·6912	39·6	40·0	−0·4
22·0	508·1	1·6928	38·8	40·0	−1·2
24·0	592·3	1·6946	38·1	40·0	−1·9
26·0	682·2	1·6963	37·4	40·0	−2·6
28·0	777·0	1·6976	36·8	40·0	−3·2
30·0	878·0	1·6992	36·3	40·0	−3·7
35·0	1154·0	1·7023	34·9	40·0	−5·1
40·0	1466·0	1·7055	33·5	40·0	−6·5

TABLE VIII.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Difference.
8·0	97·6	1·7227	26·1	25·0	+1·1
9·0	120·5	1·7264	24·5	25·0	−0·5
10·0	144·2	1·7254	24·9	25·0	−0·1
12·0	196·5	1·7233	25·8	25·0	+0·8
14·0	255·9	1·7227	26·1	25·0	+1·1
16·0	321·4	1·7219	26·5	25·0	+1·5
18·0	395·0	1·7231	25·9	25·0	+0·9
20·0	475·6	1·7245	25·3	25·0	+0·3
22·0	563·2	1·7261	24·6	25·0	−0·4
24·0	658·2	1·7278	23·8	25·0	−1·2
26·0	760·0	1·7294	23·2	25·0	−1·8
28·0	868·0	1·7309	22·5	25·0	−2·5
30·0	982·0	1·7321	21·9	25·0	−3·1
35·0	1297·0	1·7352	20·5	25·0	−4·5
40·0	1654·0	1·7383	19·1	25·0	−5·9

TABLE IX.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Difference.
8·0	104·3	1·7547	11·4	10·0	+1·4
9·0	129·3	1·7585	9·7	10·0	−0·3
10·0	155·2	1·7573	10·2	10·0	+0·2
12·0	212·5	1·7547	11·4	10·0	+1·4
14·0	277·8	1·7539	11·8	10·0	+1·8
16·0	350·0	1·7527	12·4	10·0	+2·4
18·0	431·4	1·7536	12·0	10·0	+2·0
20·0	520·9	1·7549	11·3	10·0	+1·3
22·0	618·2	1·7562	10·7	10·0	+0·7
24·0	724·1	1·7578	10·0	10·0	Nil
26·0	837·8	1·7594	9·2	10·0	−0·8
28·0	958·0	1·7605	8·7	10·0	−1·3
30·0	1086·0	1·7617	8·1	10·0	−1·9
35·0	1440·0	1·7647	6·6	10·0	−3·4
40·0	1842·0	1·7675	5·3	10·0	−4·7

TABLE X.

Correlation between Suggested V.I. and Dean and Davis V.I.

Vis. at 210° F.	Vis. at 100° F.	"n."	V.I. from "n."	Dean and Davis V.I.	Difference.
8·0	108·9	1·7749	1·6	0	+1·6
9·0	135·2	1·7787	−0·3	0	−0·3
10·0	162·5	1·7772	0·5	0	+0·5
12·0	223·1	1·7743	1·8	0	+1·8
14·0	292·4	1·7724	2·8	0	+2·8
16·0	369·1	1·7718	3·2	0	+3·2
18·0	455·7	1·7726	2·8	0	+2·8
20·0	551·1	1·7737	2·2	0	+2·2
22·0	654·9	1·7748	1·7	0	+1·7
24·0	768·0	1·7764	0·9	0	+0·9
26·0	889·6	1·7777	0·2	0	+0·2
28·0	1018·0	1·7789	−0·4	0	−0·4
30·0	1156·0	1·7801	−1·0	0	−1·0
35·0	1535·0	1·7827	−2·3	0	−2·3
40·0	1967·0	1·7854	−3·7	0	−3·7

seen that while correlation at 100 V.I. is very good, at lower V.I.s the maximum deviation increases slightly, but it is considered that even the largest deviation is such as to make no appreciable difference from a practical point of view. The reason why 100 V.I. data give such satisfactory results is that the 100 V.I. straight line in Fig. 2 is very nearly a perfect straight line, while the 0 V.I. line although straight by all practical standards is not quite so good as the 100 V.I. line. It is considered that this ties in with the remarks already made on the subject of the determination of the original L series data. The poorer correlation at 0 V.I., of course, affects all the intermediate V.I.s between 0 and 100, since these intermediate V.I.s are based on equation (1). The nature of the scale, however, shows that deviations from the Dean and Davis figures at low V.I.s are of less practical significance than those at high V.I.s. Table XI gives data obtained for viscosities at 210° F. in the range 8·0 cs.

TABLE XI.

V.I. from "n" compared with Dean and Davis V.I. for Viscosities Lower than 8·0 cs. at 210° F.

Vis. at 210° F.	Suggested Viscosity Index for Dean and Davis Viscosity Indices of—								
	0.	10.	25.	40.	50.	60.	75.	90.	100.
8·0	1·6	11·4	26·1	40·8	50·5	60·1	74·5	88·9	98·3
7·0	7·2	16·7	30·9	44·8	54·0	63·2	76·5	90·9	98·7
6·0	13·6	22·8	36·8	49·5	59·3	66·9	79·5	92·1	100·2
5·0	32·0	39·3	50·8	62·1	69·4	76·7	87·5	97·9	104·7
4·0	54·8	61·1	70·3	79·4	85·1	91·0	99·5	107·7	113·0
3·0	61·7	69·0	79·5	89·3	96·2	102·4	111·4	120·5	125·9
2·0	65·3	75·5	90·4	103·8	112·0	119·8	130·9	141·1	147·5

to 2·0 cs., and here it will be seen that considerable differences exist between the calculated V.I. and the Dean and Davis V.I. This is accounted for in Fig. 4, which shows the L and H series curves which

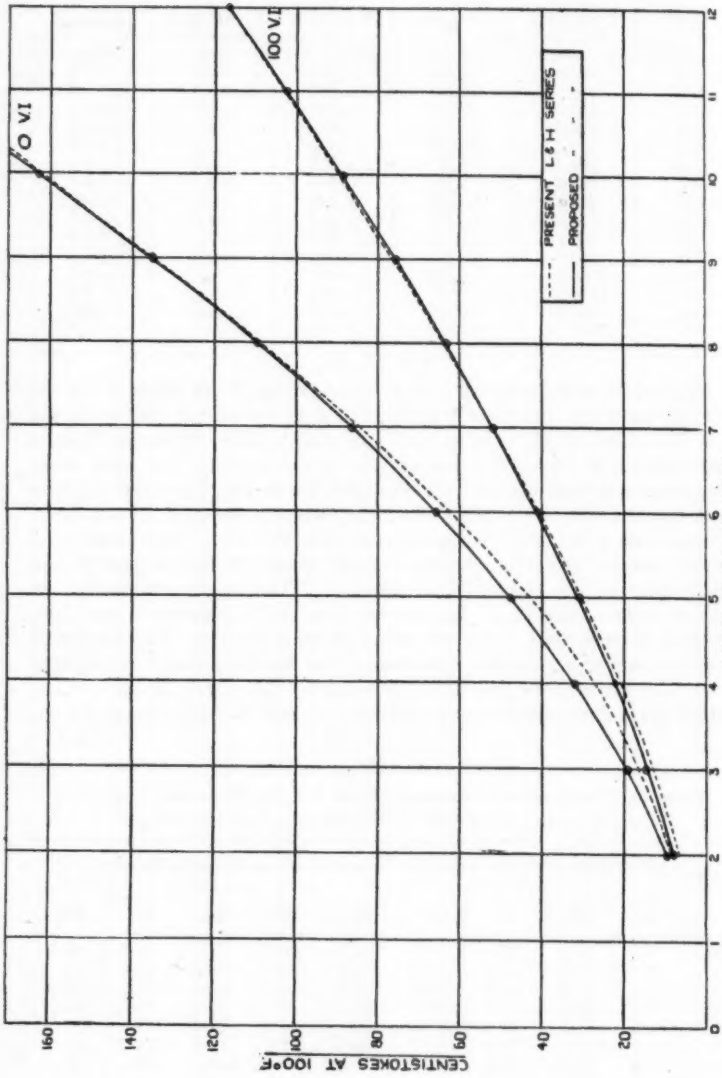

FIG. 4.

PRESENT AND PROPOSED L AND H SERIES CURVES.

would be obtained using equations (10) and (11) as compared with the arbitrary curves put forward by Dean, Bauer, and Berglund. It will be

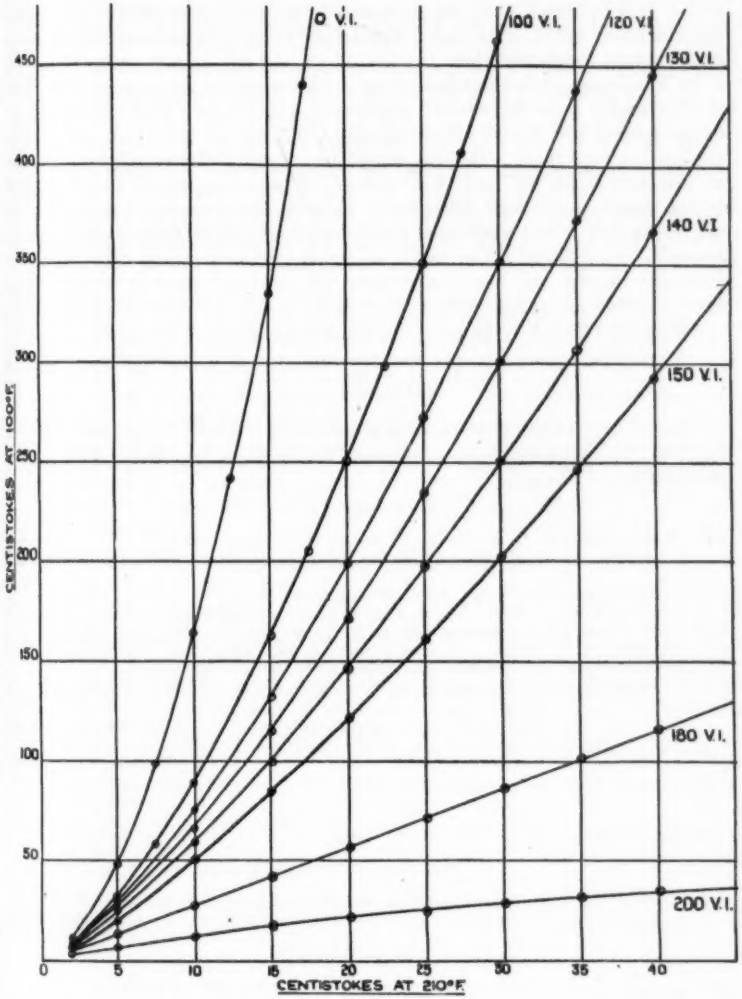

FIG. 5.

PROPOSED NEW VISCOSITY INDEX SYSTEM.

seen that the H curve deviates slightly from the present curve, while the L curve deviates considerably. It is of interest to note that the H curve put forward by Fenske and co-workers is very close to the H curve produced from equations (10) and (11).

PRESENT AND PROPOSED L AND H SERIES CURVES.

With regard to the already described anomalies at high viscosity indices in the present Viscosity Index system, Fig. 5 illustrates quite clearly the nature of the proposed new system; it is in marked contrast with Fig. 1, and it will be noted that the proposed new system completely eliminates the anomalies referred to, and is applicable to an infinite range of viscosity temperature characteristics.

In conclusion, it is suggested that the Viscosity Index system described in this paper provides several important advantages, while the mass of experimental and routine data already built up on the Dean and Davis system between 0 and 100 V.I. would be substantially unaffected, except at low viscosities and low V.I. values. The extension of the Viscosity Index system to include oils of any viscosity–temperature characteristics satisfies a felt want, and since it appears likely that this system can be extended to include those products having viscosities at 210° F. lower than 2·0 cs., by the use of any two temperatures instead of two fixed temperatures as at present, a new field would thereby be opened up which could materially increase our knowledge of these products.

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THE PROBLEM OF ENGINE DEPOSITS.

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SUMMARY.

A description of rheological methods found useful in investigating the problem of engine deposits is given.

1. Measurements have been made of the specific viscosity of (*a*) dispersions of aero-engine deposits and oxidized oil products to determine molecular weights and asymmetry of the constituent particles and (*b*) of carbon dispersions in oils and non-aqueous media to measure the degree of flocculation.

2. The flow behaviour of mineral oils oxidizing at high temperatures has been studied, using a coni-cylindrical rotor fitted with small vanes immersed in the oil and operated by weights acting over a pulley. It has been found that rigidity developed slowly at first with time, then the oxidizing oil suddenly gelated when the concentration and degree of polymerization of the oxidized products reached a critical value. This behaviour was confirmed by measurements made with a tackmeter.

3. The tendency of an oil to deposit soot and other combustion detritus in suspension has been measured from (*a*) torsional rigidity and yield values and (*b*) sedimentation rates and volumes. In general, a high degree of flocculation of carbon black, etc., results in high specific viscosity, high sedimentation rates and volumes, and high rigidities and yield values of the suspensions.

Definitions and Symbols Used.

1. *Relative viscosity* is η/η_0, where η is the viscosity of a sol or suspension and η_0 that of the dispersion medium.

2. *Specific viscosity*, $\eta_{sp.}$, is $\dfrac{\eta - \eta_0}{\eta_0}$ or $\eta/\eta_0 - 1$.

3. *Intrinsic viscosity* is the specific viscosity divided by the concentration $\eta_{sp.}/C$, and the limiting intrinsic viscosity $[\eta]$ is the viscosity at zero concentration. A convenient method of making short extrapolation to zero concentration is by dividing the logarithm of relative viscosity by concentration (Kraemer).

4. *The proportionality constant*, $K_{cm.}$ (Kraemer), is the limiting intrinsic viscosity divided by molecular weight.

5. *The partial specific volume*, $\bar{v}$, is the volume increment of a dispersion for 1 gram of dispersed phase.

6. *The shape factor*, ν, $\nu = \dfrac{100[\eta]}{\bar{v}}$. For spherical particles, from Einstein's equation, $\eta = \eta_0(1 + 2{\cdot}5\phi)$, the value of ν is 2·5, or, $\nu = \dfrac{1}{\phi}(\eta/\eta_0 - 1)$.

7. *Yield value* has been expressed as the minimum number of grams required to begin movement of the cylinder immersed in a suspension in a Stormer type of viscometer.

THE approach to the problem of engine fouling with ring sticking, etc., due to carbonaceous deposits can well be made by rheological methods, and the purpose of this paper is to present these methods, with a *résumé* of some results obtained.

As the title suggests, we have confined our study to the problem of the deposition of oxidation and combustion products of oil and fuel in aero engines, for the efficient functioning of which it is considered necessary to assess the tendency of oils to deposit their load of soot or carbon black,

oil oxidation products, and other detritus. All these can cause the sticking of rings and valves, plugging of oil-holes and filters, and crankcase sludging, thus reducing the useful life of an engine.

For convenience the paper has been divided into three parts. Part 1 deals with the colloidal character of the deposits in relation to our knowledge of bituminous substances; Part 2 describes a method of following the rheological behaviour of an oxidizing oil at a high temperature; and Part 3 deals with methods of measuring the capacity of an oil to disperse and hold micro particles in suspension.

Part 1. The Colloidal Character of Oil-Oxidation Products.

Oil deterioration in engines results from the oxidation of the hydrocarbons at hot surfaces and from the thermal decomposition of the hydrocarbons and their oxidation products; while instability towards oxidation reduces the useful life of an oil, decomposition of the oxidation products causes such troubles as ring-sticking.

Considerable literature exists on the subject of oil deterioration, but there is little knowledge of the nature of the deterioration products themselves, beyond a shrewd guess that they are complex colloidal bodies, possibly produced by polymerization and condensation.

Oil-oxidation products can be separated into many fractions by selective solvent action; this method was used in an attempt to classify the engine deposits by fractionation with a range of solvents increasing in polarity, surface tension, internal pressure, etc. More recently we have developed with some success ultra-chromatographic technique for the separation of oil-oxidation products, and there is hope that a number of fractions will yield substances that can be identified.

Molecular weights and the asymmetry of the colloidal particles were determined from viscosity measurements.

Experimental.

A mineral aero-engine oil was oxidized at 250° C. for 15 hours, and the resulting asphalt was extracted first with petroleum ether and then with benzene. The benzene extract was then chromatographed on a silica gel column and separated into some thirty fractions by elution with solvents of increasing activity in the following order: petroleum ether, petroleum ether plus 10 per cent. benzene, benzene, benzene plus 5 per cent. ethyl alcohol, chloroform, benzene plus methyl alcohol, carbon disulphide saturated with methyl alcohol, pyridine plus carbon disulphide with methyl alcohol. The zones developed by each eluent were eluted from the column with reference to their banding and fluorescence in ultra-violet light. For further work these eluates were repeatedly chromatographed on other adsorbents, such as, for example, activated alumina, magnesia, etc.[1] The samples referred to in this paper were obtained by primary separation from the silica-gel column, chosen to represent the whole of the benzene soluble series. Fraction 1, mentioned in Table 1, was obtained by elution with benzene and ethyl alcohol, fraction 2 with chloroform, and fraction 3 with carbon disulphide and methyl alcohol. The intermediate fractions were omitted for the time being.

The specific viscosities of the samples were determined with an efflux type of viscometer, as shown in Fig. 1, at 20° C., using a capillary bore of about 0·5 mm.

The well-known Einstein equation :—

$$\eta = \eta_0(1 + 2{\cdot}5\phi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

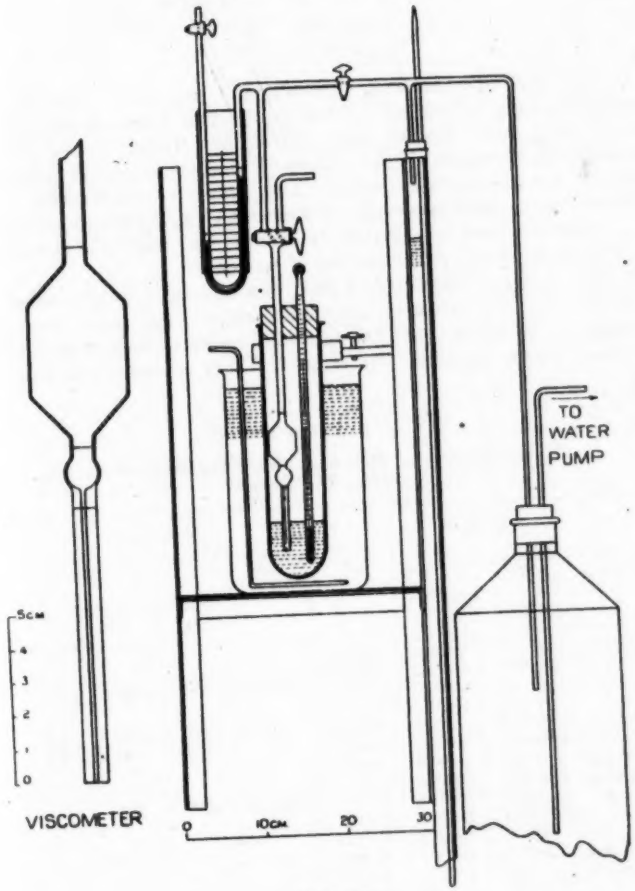


FIG. 1.

SET-UP OF PLASTOMETER.

where η is the viscosity of a suspension of spheres, η_0 the viscosity of the suspending medium, and ϕ the volume per c.c. of the dispersed phase was modified by Staudinger to give a direct relationship between specific viscosity and molecular weight of high polymers :—

$$\eta_{sp.}/C_{gm.} = K_m M \text{ or } [\eta] = K_m M \quad . \quad . \quad . \quad . \quad (2)$$

where $C_{gm.}$ is the concentration in molarity of the polymeric unit (base molarity) and $K_{m.}$ is the proportionality constant.

Kraemer[2] has further modified this formula using concentration by weight, so that, knowing the proportionality constant $K_{cm.}$, the molecular weight of the substance can be calculated from the specific viscosity data, or vice versa, from the following formla :—

$$\frac{\log \eta/\eta_0}{c} = K_{cm.}M \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In our work the molecular weight by cryoscopy in benzene and the specific viscosity in benzene solution for fraction 1 were at first determined and the K_{cm} value for the series calculated. It was considered that if the asphaltic products are substances of kindred polymeric character (iso-colloids), the rheological constants determined for one fraction should be applicable to another, especially for molecular-weight determinations. This $K_{cm.}$ value was used to calculate the molecular weights of the other fractions from their specific viscosities in benzene.

It will be seen from Table I that the molecular-weight values found from the specific viscosity compare closely with those measured by cryoscopy. It follows that the fractions under examination belong to a polymeric series, for which the proportionality constant was $3{\cdot}74 \times 10^{-5}$.

TABLE I.

Results Obtained for Molecular Weight and Shape of Particle.
$K_{cm.}$ $3{\cdot}74 \times 10^{-5}$.

Description of Sample.	Conc., gr.	Log η/η_0.	$[\eta]$.	$[\eta]$, aver.	Molecular Weight by—		ν.	Axial Ratio.
					Viscosity.	Cryoscopy.		
Fraction 1	0·351	0·0066	0·0188					
	0·604	0·0132	0·0219	0·0206	550	548	4·5	*c.* 4
	0·806	0·0183	0·0227					
	1·010	0·0191	0·0189					
Fraction 2	0·402	0·0076	0·0189	—	505	496	4·4	*c.* 4
Fraction 3	0·126	0·0045	0·0357	—	955	1024	2·6	*c.* 1·5
Aero engine oil (fresh)	0·510	0·0064	0·0125					
	0·770	0·0098	0·0127					
	1·020	0·0128	0·0125	0·0125	334	345	—	—
	1·980	0·0249	0·0126					
	3·060	0·0378	0·0124					
After 5 hrs. oxidation	0·301	0·0072	0·0240					
	0·602	0·0132	0·022					
	1·000	0·0230	0·0230	0·0237	634	648	—	—
	1·40	0·0346	0·0247					
	2·003	0·0500	0·0250					
After 11 hrs. oxidation	0·180	0·0076	0·0422					
	0·492	0·0191	0·0389					
	0·720	0·0278	0·0386					
	0·970	0·0367	0·0378	0·0394	1053	—	—	—
	1·31	0·0518	0·0395					
	1·67	0·0660	0·0395					
	1·93	0·0766	0·0396					

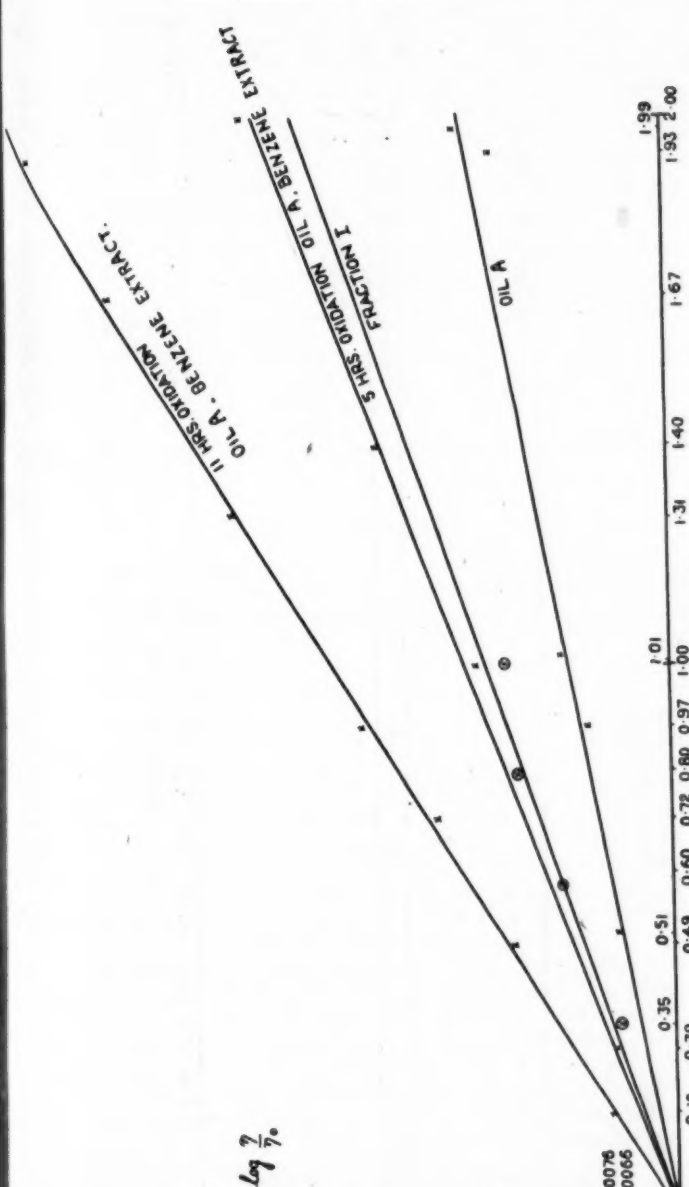

OIL A. 11 HRS. OXIDATION. BENZENE EXTRACT.
OIL A. 5 HRS. OXIDATION. BENZENE EXTRACT.
FRACTION I
OIL A
Log I/I₀
0·0766
0·0660
0·0518
0·0500
0·0367
0·0346
0·0278
0·0230
0·0191
0·0183
0·0132
0·0076
0·0066
0·0072
0·18
0·30
0·35
0·49
0·51
0·60
0·72
0·80
0·97
1·00
1·01
1·31
1·40
1·67
1·93
1·99
2·00
CONCENTRATION GRMS/100 CC.

FIG. 2.

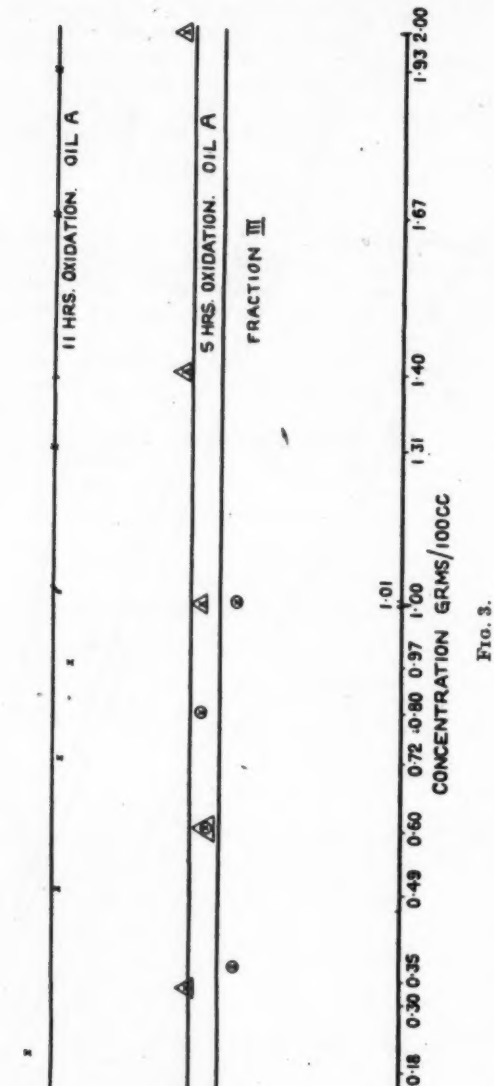

11 HRS. OXIDATION. OIL A
5 HRS. OXIDATION. OIL A
FRACTION III
VISCOSITY
INTRINSIC
0·0396
0·0219
0·0188
0·0227
0·0206
0·18 0·30 0·35 0·49 0·60 0·72 0·80 0·97 1·00 1·01 1·31 1·40 1·67 1·93 2·00
CONCENTRATION GRMS/100CC

FIG. 3.

It was found that this $K_{cm.}$ value was valid for the oil itself and the ordinary benzene extracts of the oil at different stages of oxidation.

It was considered that the shape factor ν would afford some knowledge of the change in shape and size of the particles with increasing polymerization. This factor is calculated from the well-known Jeffrey's equation based on deviations from the Einstein coefficient, which is 2·5 for spherical particles. The coefficient obtained from the specific viscosity measurements of the oxidized oil products in benzene was at first calculated from the partial specific volume by the following equation :—

$$\frac{[\eta]}{\nu} = \frac{\bar{V}}{100} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\bar{V}$ is the partial specific volume. The axial ratios were then obtained from the Jeffery [3] equation :—

$$\nu = \frac{J}{\text{arc tan } J} \cdot \frac{16}{15} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where J is the axial ratio of the major to minor axes of the ellipsoid.

Discussion.

Although Staudinger's rule has been criticized, its validity appears to depend on whether intrinsic viscosity is independent of concentration and whether the relative viscosities of the solutions are in linear relation to the concentrations of the solute. In Figs. 2 and 3 it is shown that these conditions are satisfied both for the chromatographically separated fractions and for the solvent extracts of the oil oxidation products.

The early classification of colloids into lyophilic and lyophobic classes is based chiefly on the behaviour of the colloid towards the dispersion medium, but more recent studies of high polymers based on the structure of the colloidal particles have led to further classifications—namely, suspensoids and emulsoids, associated or micellar colloids, and molecular colloids.[4] The viscosities of colloidal solutions depend not only on the structure, but also on the shape of particles. It is possible to distinguish between solutions of spherical particles and elongated particles. The viscosity of the first is relatively low, and is in accord with Einstein's equation, and is independent of the degree of dispersion.

The closeness of the values found for ν in the case of bitumen fractions to the Einstein coefficient of 2·5 indicates that these substances belong to the borderline cases of suspensoids, emulsoids, and micellar colloids. The micellar colloids, because of their shape, resemble macromolecular particles, and the flow of their dispersions is not in accord with Poiseuille's equation. The micellar colloids differ from the molecular colloids in that their solutions behave differently with temperature change because of the structure of the particles. The specific viscosities of solutions of molecular colloids is little affected by temperature because the atoms in the colloidal particles are linked by covalencies.[4] With micellar colloids, however, the structure disappears at higher temperatures, as the weaker intermicellar forces are easily overcome; the viscosity change is therefore reversible.

The use of selective solvents on micellar bituminous products separates them into alpha, beta, and gamma fractions with reference to their intermolecular forces.[5] This is supported by the fact that however carefully

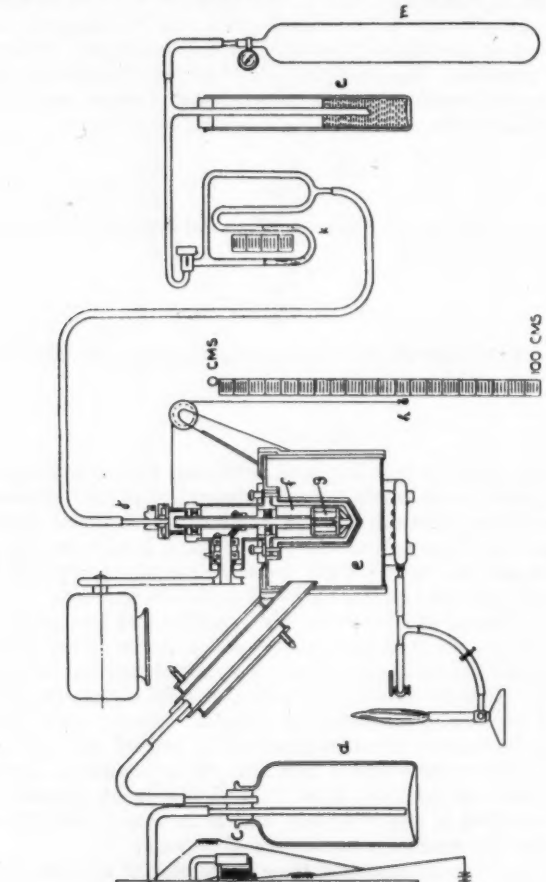


FIG. 4.
HIGH TEMPERATURE VISCOMETER.

extracted the fractions may be, on chromatography of the fractions on suitable media, a large number of the constituents are found to be identical or similar.

The axial ratios determined for the fractions show that with increasing degree of polymerization the shape of the molecules tend to be globular rather than ellipsoidal. This perhaps can be explained by Houwink's hypothesis that with increasing degree of polymerization some polymers tend to close the chain by "cyclization." Our results are in line with the general supposition that asphaltene micelles are globular or globularly coiled, a conclusion arrived at by various rheological methods of examining asphaltic products.

The above conclusions about the colloidal nature of the oil oxidation products will have bearing on what follows in Part 2, where the viscosity behaviour of oxidizing oils is discussed.

Part 2. A Rheological Study of Oxidizing Oils at High Temperatures.

The use of rotational types of viscometers where the rate of shear can be varied is well known. The Stormer type has been widely used to test paints, etc. Pfieffer and Van Doormal [6] have referred to the use of the "Wolff-Hoepke Turboviscometer" for the study of gelation in asphaltic bitumen solutions at moderate or low temperatures.

For the study of the oxidation kinetics and the rheological behaviour of aero engine lubricating oils it was considered necessary to

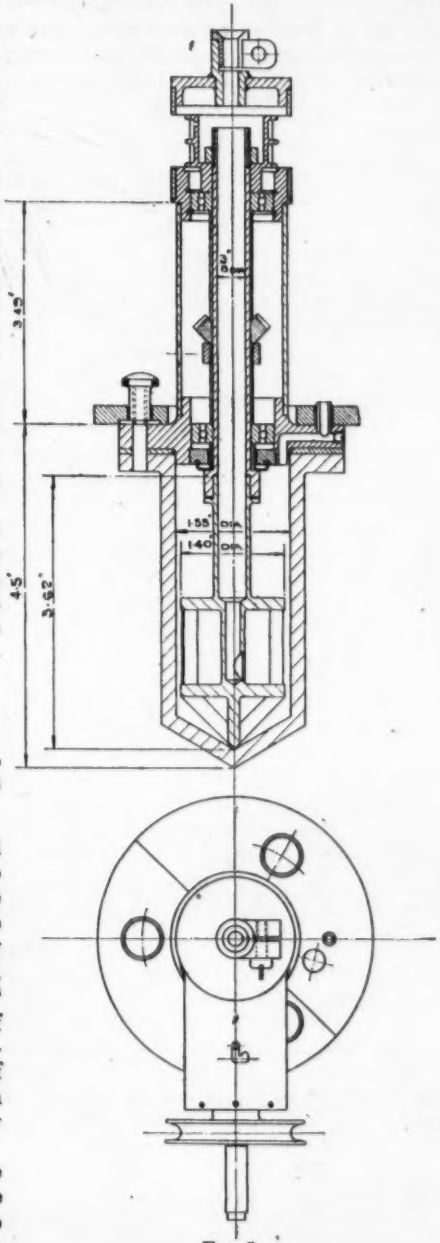


Fig. 5.
HIGH TEMPERATURE VISCOSITY METER.

investigate these characteristics at higher temperatures approaching the conditions in the engine itself (200–300° C.). A special viscometer (Figs. 4 and 5) was therefore designed in which simultaneous oxidation and viscosity measurements could be carried out at high temperatures. The combination of viscometer and the oxidation bath consists essentially of a coni-cylindrical stainless steel cup and a special type of stirrer which is also coni-cylindrically shaped and pivoted in the bottom of the cup. The axis of the stirrer is hollow and coupled to the main driving-shaft by a male-female joint. The driving shaft is also hollow, so that either an oxygen inlet tube or a thermometer can be introduced into the cup. The results reported in this paper were obtained by using a bladed form of stirrer, although a cylindrical stirrer was also used; the results were similar for both stirrers. The set-up of the apparatus is shown in Fig. 4. The steel cup is placed in the coni-cylindrical hollow of a well-lagged steel mercury vapour bath. For accurate temperature control to within 0·1° C. the mercury vapour bath is connected to a Hyvac pump via several pressure stabilizers, and the vacuum is controlled by a solenoid-operated air-leak. The desired temperature is then obtained by adjusting the boiling point of mercury. For temperatures below 210° C. other suitable substances are used in the bath. The heating is carried out by a gas ring-burner controlled by a needle valve. A weighed amount of oil, sufficient to cover completely the stirrer throughout the test (about 60 ml.), is poured into the cup. Oxygen is introduced at the rate of 15 litres an hour through an oxygen inlet tube which passes through the hollow of the shaft and stirrer. During oxidation the oil is kept stirred by connecting the pulley on the side of the shaft with a slowly rotating motor. The pulley which is geared to the shaft can be completely detached by pushing a sliding pin. The flow of pure oxygen is adjusted by a pressure stabilizer and a delicate needle valve.

At the end of a period of oxidation, the oxygen inlet tube is withdrawn and an accurate thermometer introduced into the oil. A known load is suspended from the string passing over the pulley. The time of fall of the weight against a scale is then measured; a height of 50 cm. is convenient. The viscosity is proportional to :—

$$\frac{\text{wt. in gm.} \times t \text{ in seconds}}{50 \text{ cm.}}.$$

The advantage of this type of viscometer is that the material under test can be deformed or made to flow under different shearing stresses by simply altering the load.

If the viscosity readings are plotted against the rates of fall with different loads, a viscosity behaviour curve is then obtained as illustrated in Fig. 6, the shape of the curve depending on whether the material under test is strictly Newtonian or possesses rigidity. With oils a straight line parallel to the velocity axis is usually obtained, while for materials exhibiting plastic flow a sloping curve is obtained. The slope of this curve, tan α, is an approximate and convenient measure of the rigidity of the system.

$$\text{Tan } \alpha = \frac{\text{viscosity}_1 - \text{viscosity}_2}{\text{rate}_2 - \text{rate}_1}$$

where viscosity$_1$ was obtained with a load giving rate$_1$ and viscosity$_2$ obtained with the load giving rate$_2$.

The rheological behaviour of the substance may now be studied in terms of the viscosity value obtained at a given rate of shear and tan α. Although the data presented here give a sloping curve for the plastic flow, it has been found that plotting on a double logarithmic basis gives rectilinear relationship between the viscosity and the rate of fall, but a number of irregularities are removed which in themselves may be interesting.

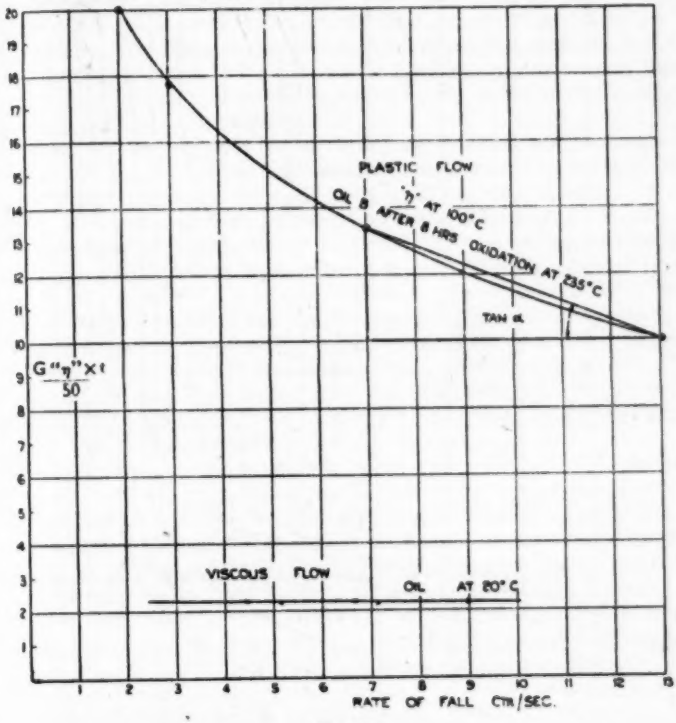


FIG. 6.

It can be emphasized here that the instrument was designed as a research tool to study complex flow behaviour rather than to obtain measurements of the absolute viscosity. The kind of information that can be obtained is given in Table II, where the flow behaviour of two oxidizing oils is compared. The oils were oxidized at 235° C., using fresh oil for each period of oxidation. After each period of oxidation viscosity measurements were made over a range of temperature from 20° C. to 235° C. using two different rates of shear which were respectively the same throughout the temperature range; the data are given in graphical form in Fig. 7. At high temperatures, when the viscosity of the oil was very

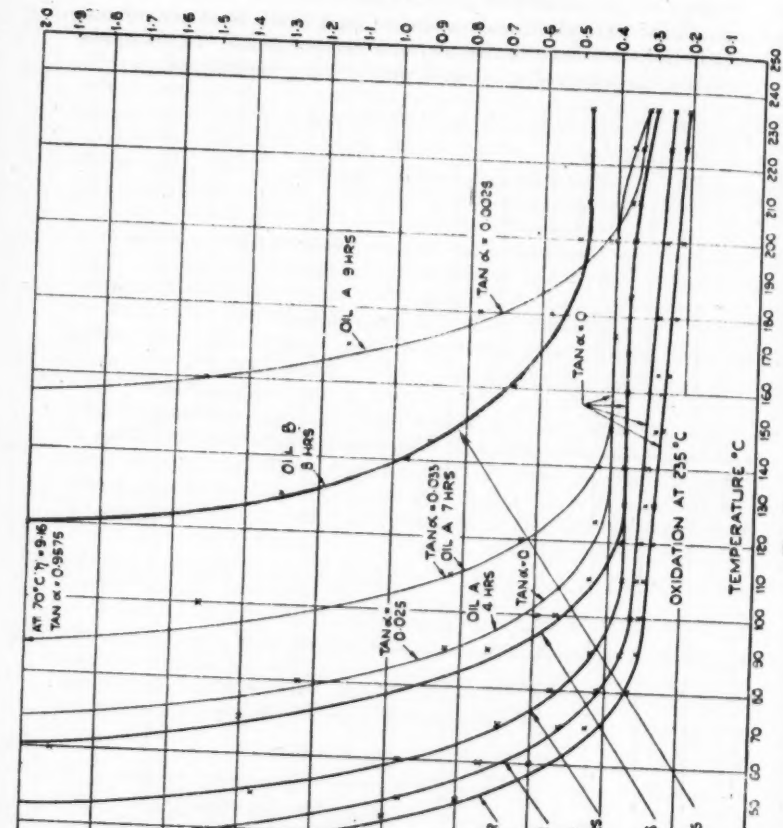

AT 70°C η = 9·16
TAN α = 0·9575
OIL B 8 HRS
OIL A 9 HRS
TAN α = 0·0328
TAN α = 0·033
OIL A 7 HRS
TAN α = 0·025
OIL A 4 HRS
TAN α = 0
OIL B 0 HR
OIL B 1 HR
OIL B 2½ HRS
OIL B 5 HRS
OIL B 8 HRS
OXIDATION AT 235 °C
TEMPERATURE °C
G "η" X t / 50

Fig. 7.

DEVELOPMENT OF RIGIDITY AND VISCOSITY—TEMPERATURE CHARACTERISTICS IN OXIDIZING OILS.

small, turbulence was sometimes indicated by a negative value of tan α. The rates of shear giving turbulence were avoided.

Discussion of Results.

It will be seen from the curves in Fig. 7 that at higher temperatures there is little difference in viscosity with time of oxidation. The viscosity rises at first, slowly attaining a maximum, then eventually a crisis is reached when the oxidizing oil gelates to a solid. This is rather remarkable, as it will be seen from the curves that considerable differences in viscosity behaviour exist at lower temperatures. For each oil and for each period of oxidation there is a critical temperature range when differences in viscosity can be detected as shown by the swinging of the curves from the horizontal to the vertical.

Lubricating oils for aero-engine cylinders function at temperatures between 200° and 300° C., so the effect of oxidation over a period of time at these higher temperatures would seem to make little difference to the viscosity, and with two fresh lubricating oils the difference in viscosity at 300° would be vanishingly small. B. V. Losikov and colleagues [7] carried out viscosity measurements with cylinder oils and oil and asphalt mixtures from 100° C. to 350° C. using an Ostwald type of viscometer. They found that with increasing temperature there was a gradual approach to a common viscosity. Thus with an oil–asphalt mixture and the oil itself a difference of 340 per cent. was measured at 100° C., while at 216° C. it was only 20 per cent., and at 345° C. it was practically nil. The question now arises, By what physical criterion can a lubricating oil be judged for service at high temperatures?

A study of the curves in Fig. 7 shows that although the viscosity remains the same with time of oxidation at higher temperatures, a critical point is reached when there is an abrupt change in viscosity even at high temperatures. This point of change is dependent on the type of oil, the time and temperature of oxidation, and on the temperature at which the viscosity is determined. Oil A, for example, having reached a maximum viscosity at high temperatures at the end of 4 hours of oxidation, maintains the same viscosity above 200° C. for a further period of 9 hours of oxidation. Oil B, on the other hand, reaches a maximum viscosity after 2½ hours of oxidation, remains the same up to 5 hours, and after 8 hours of oxidation thickens abruptly to an asphaltic mass. Oil A reaches this point well after 11 hours of oxidation. The feature which changes regularly with time of oxidation is the critical temperature range over which the viscosity–temperature curves swing to the vertical. For an initial period the curves are parallel; it is difficult to say whether this is due to partial volatilization of the oil or to an induction period of oxidation. The condition of the oil represented in the horizontal part of the curve is that of a true solution, the value of tan α being nil. When the curve swings to the vertical, the values of tan α become positive; in other words, the systems cease to be truly Newtonian and exhibit some rigidity. The rigidity which sets in at this critical temperature range increases further with lowering of temperature. This critical temperature range can therefore be called the gelation period, for below it the systems

FIG. 7. DEVELOPMENT OF RIGIDITY AND VISCOSITY–TEMPERATURE CHARACTERISTICS IN OXIDISING OILS.

behave as gels. Even some fresh oils (Oil B) show this rigidity at ordinary temperatures, although the values of tan α in these cases are extremely small. It will also be seen from Table II that with increasing time of

TABLE II.

(*a*) *Oil A*: η^* 100° *F.* = 276·1 *cs.*; η^* 210° *F.* = 20·2 *cs.* *Oxidised at* 235° *C.*

Hrs. of Oxidation. *T* °C.	0.		4.		7.		9.		11.	
	"η"	tan α.	"η"	tan α.	"η"	tan α.	"η"	tan α.	"η"	tan α.
235	0·24	0	0·32	0	0·32	0	0·32	0	3·0	—
225	0·24	0	0·36	0	0·36	0	0·32	0	—	—
210	0·25	0	0·36	0	0·38	0	0·36	0	—	—
200	0·26	0	0·40	0	0·40	0	0·42	0	—	—
190	0·28	0	0·40	0	0·40	0	0·56	0	—	—
180	0·28	0	0·40	0	0·40	0	0·78	0	—	—
170	0·28	0	0·40	0	0·40	0	1·14	0·0028	—	—
160	0·29	0	0·40	0	0·40	0	1·53	0·023	—	—
150	0·29	0	0·40	0	0·40	0	—	—	—	—
140	0·29	0	—	—	0·42	0	—	=	—	—
120	0·31	0	125C 0·44	0	0·64	0·0041	—	—	—	—
110	0·32	0	—	—	0·82	0·0098	—	—	—	—
100	0·32	0	0·60	0·0043	1·52	0·033	—	—	—	—
90	0·33	0	0·84	0·012	2·46	0·072	—	—	—	—
80	0·36	0	1·24	0·025	4·24	0·258	—	—	—	—
70	0·42	0	—	—	9·60	0·9375	—	—	—	—
60	0·54	0	—	—	—	—	—	—	—	—
50	0·74	0·0001	—	—	—	—	—	—	—	—
20	2·2	0·0005	13·4	0·12	333·8	—	1092	—	—	—

(*b*) *Oil B*: η^* 100° *F.* = 269·5 *cs.*; η^* 210° *F.* = 20·30 *cs.* *Oxidised at* 235° *C.*

Hrs. of Oxidation. *T* °C.	0.		1.		2½.		5.		8.	
	"η"	tan α.	"η"	tan α.	"η"	tan α.	"η"	tan α.	"η"	tan α.
235	0·21	0	0·25	0	0·30	0	0·30	0	0·48	0
225	0·21	0	0·26	0	0·30	0	0·30	0	0·48	0
200	0·22	0	0·26	0	0·36	0	0·36	0	0·50	0
190	0·22	0	0·26	0	0·36	0	0·36	0	0·54	0
180	0·22	0	0·28	0	0·36	0	0·36	0	0·56	0
165	0·25	0	0·28	0	0·36	0	0·36	0	0·58	0
150	0·26	0	0·29	0	0·36	0	0·36	0	0·76	0·002
140	0·27	0	0·30	0	0·36	0	0·36	0	0·96	0·009
130	0·28	0	0·30	0	0·36	0	0·36	0	1·30	0·027
120	0·28	0	0·30	0	0·36	0	0·38	0·002	2·08	0·045
110	0·30	0	0·32	0	0·36	0	0·46	0·005	2·30	0·067
100	0·30	0	0·33	0	0·39	0·001	0·53	0·021	—	—
90	0·32	0	0·41	0·001	0·44	0·005	0·72	0·052	10·4	0·872
80	0·34	0	0·42	0·004	0·54	0·008	1·04	0·091	—	—
70	0·45	0	0·58	0·006	0·68	0·021	1·40	0·102	—	—
60	0·60	0·001	0·90	0·029	0·96	0·043	1·92	0·139	—	—
50	0·80	0·005	0·96	0·031	1·36	0·092	3·24	0·156	—	—
45	1·04	0·006	—	—	—	—	—	—	—	—
40	1·18	0·025	—	—	2·48	0·140	—	—	—	—
35	1·39	0·028	2·32	0·052	—	—	—	—	—	—
25	1·77	0·037	—	—	—	—	—	—	—	—
20	1·95	0·040	—	—	—	—	—	—	—	—

* By suspended level viscometer.

oxidation a rigidity appears at higher temperatures and that the degree at the same temperature also increases appreciably. This process of gelation at higher temperatures continues until, after a time of oxidation that is characteristic of the oil, the whole system behaves as a solid gel at the temperature of the test. At lower temperatures (20–100° C.) the viscosity change and the degree of plasticity with oxidized oils can be so large that it is scarcely practicable to measure them or to attempt to characterize different oxidized oils by this means. It may be of interest to note that Oils A and B are quite different in their behaviour in an engine. Oil A in comparison with Oil B proved to be bad from the point of view of ring-sticking and engine cleanliness when tested on air-cooled single-cylinder-test engines. Much more work, however, must be done before it is possible to generalize on this point.

In attempting to explain the phenomena it is emphasized that our work is incomplete and that only tentative explanations can be put forward.

The plasticizer in a gel will have an important effect on the rheological behaviour of the system. The colloidal system of an oxidized oil may be classified into three parts: (*a*) the dispersion medium consisting of the oil, (*b*) the protective colloids such as oil soluble resins, and (*c*) the dispersed phase of asphaltenic products. It has been shown by various workers [6, 8, 9, 10, and 12] that the flow properties depend on the interrelation of these three parts. When the asphaltenic micelles are peptized by the influence of the protective colloids, the system behaves like a truly liquid material. When, however, the protective colloids are absent or have been destroyed by oxidation, the system exhibits rigidity, the degree rising with decreasing peptization of the micelles. The increase in rigidity with time of oxidation is therefore understandable. The critical temperature range and time of oxidation at which the oxidized oil behaves as a gel must therefore be due to some abrupt change in the relation between the components of the colloidal system. Asphaltenes are lyophilic towards aromatic substances, so the change in an undoped oil may be partly governed by the stability of some naturally occurring aromatic type of substances that are relatively more resistant to oxidation.

In Part I of this paper we have already discussed the nature of the dispersed phase, and have pointed out that with micellar colloids an increase in temperature results in the destruction of the micellar structure. The fact that at higher temperatures the viscosity is apparently independent of the time of oxidation up to the critical period can perhaps be explained on this basis, the oxidized oil polymers being in solution. With lowering of temperature at first incipient gel formation occurs, and finally all the dispersed phase becomes aggregated in the gel structure. The gelation temperature is governed not only by the concentration of the dispersed phase, but also by the size and shape of the particles. It will be seen from Table I (Part 1) and Fig. 2 that the specific viscosities, and therefore the particles size and calculated molecular weights, of the benzene extracts of the oxidized oil sample increase considerably with time of oxidation. The average size of the particles after 11 hours of oxidation is nearly three times that of the particle in the fresh oil, and the increase is regular with time of oxidation. This also corresponds with the increase in rigidity at lower temperatures and with the onset of rigidity at higher temperatures.

Each of the viscosity–temperature curves can be split into two linear portions, one below and one above a certain temperature range, which is a function of the time of oxidation under the conditions of the experiment, and has been termed by Houwink [11] the "transformation interval." He points out that this phenomenon occurs with other materials such as glass (500–700° C.), and on the basis of the Andrade formula $\left(\eta = Ae^{\frac{-B}{T_{abs.}}}\right)$ the interval is often considered to be due to "an extensive change in association" and by Houwink to the assumption of the gel state by the material.

In this discussion we have not considered the change in the nature of the residual oil after oxidation forming the plasticizer. Nor have we discussed whether only part of the original oil is oxidized and the remainder more or less unchanged until a critical time and temperature of oxidation have been reached. The whole effect is very complex, and much more work is necessary to explain fully the features that have been observed by a rheological study. In Table III are given the yield values for Oil A

TABLE III.

	Minimum Breaking Loads in gms.
Oil A : Oxidized at 200° C. (B.A.M. test) :	
Fresh oil	6·5
10 hrs. oxidation	7·5
30 „ „	8
40 „ „	10
Oil A : Oxidized at 235° C. with 15 litres of oxygen per hour :	
5 hrs. oxidation	10
11 „ „	Exceeding > 250

measured at 20° C. by the tackmeter method described in Part 3 for various periods of oxidation at two temperatures. Good agreement was obtained for yield values determined by the viscometer described in this part and by the tackmeter method.

All the points not discussed here are subjects for further investigation.

PART 3. THE FLOCCULATION AND SEDIMENTATION OF MICRO-PARTICLES IN MINERAL OILS.

One of the desirable qualities of an engine oil is to retain in suspension particles of soot and other detritus that might foul an engine if deposited on its internal surfaces; an oil which is a good dispersive medium for micro-particles may not have detergent action in the chemical sense of being able to remove surface deposits already formed, but it can retain in suspended form further detritus and tend to disperse any deposits which by thermal or mechanical action become detached.

The problem in hand is to devise suitable quantitative methods for assessing the capacity of an engine oil to suspend micro-particles with a view to finding the oils which have the greatest capacity for carrying away their own decomposition products, soot, etc., so minimizing deposits

and interference in normal engine operation. Some oils undoubtedly can retain carbon black, graphite, quartz particles, etc., in suspension better than others; thus, for example, a small proportion of carbon black suspended in Pennsylvanian cylinder oil or castor oil may show little or no separation on standing, while in other oils flocculation and sedimentation can occur in a few hours or days, leaving a clear layer of oil above the black loose sediment. Talley and Larsen [13] have described filtration tests through asbestos of oils containing added asphaltenes, assessing the detergency of an oil by the amount of asphaltene carried through the filter.

Flocculation of micro-particles in liquid media occurs to a greater or less extent spontaneously with time in suspensions even at low concentrations.

Observers have watched under the microscope the growth of clusters of individual particles followed by secondary aggregation of these clusters into a network intermeshed with channels and free dispersing medium. Often the particles form skeletal chains, and may overlap, but no definite geometrical alignment of flocculated particles is detectable, and the particles that have ceased to move seem to be clearly separated by a liquid film of about 2 or 3 Å. in thickness.

The process of flocculation is reversible to some extent by shaking or stirring (thixotropy), when the particles become separated and the system tends to become more fluid and Newtonian in character.

It has been reported by Arnold and Goodeve,[14] McDowell and Usher,[15] that a newly-formed carbon suspension may not conduct electricity, but it appears to do so after an interval of time when a continuous network of carbon particles has been formed.

The rate of flocculation, as in the case of coagulation, appears to be directly proportional to the number of particles present and inversely proportional to frictional resistance, but in flocculation not all collisions are effective, as appears to be assumed in the process of coagulation when the forces of attraction are stronger.

Thixotropy is generally more pronounced with asymmetric particles such as those of carbon black, bentonite clays, etc.; contributory causes to this are the shorter average minimum distance between the particles and the greater overlap and area of contact possible. Carbon-black particles examined by the electron microscope appear to be spheroidal in shape and of size 25–300 μμ; [16] they have also been described by Arnold and Goodeve [14] as plate-like with strong valency forces around the edges.

The fundamental causes of flocculation in non-aqueous media are not clearly understood; thus Soyenkoff [17] concluded that the stability of colloidal graphite is not related to the particle charge, and Kruyt,[18] in dealing with the problem of stability of colloidal suspensions, stated, "All our results are confined to an ionizing intermicellar liquid and I can scarcely think of any satisfactory way of extending these discussions to non-aqueous systems."

The methods adopted and described in brief in this note to determine the degree of flocculation of micro-particles in various oils are the determination of (i) the specific viscosity of suspensions, (ii) the rate of sedimentation and volume of sediment, and (iii) the degree of rigidity, yield value, and thixotropy of the suspensions.

FIG. 8.

THE SPECIFIC VISCOSITY OF CARBON BLACK SUSPENSIONS IN OILS.

In general, when the degree of dispersion is high, the degree of rigidity, the specific viscosity, the rate of sedimentation, and volume of sediment are low, while, on the other hand, when flocculation has occurred, the specific viscosity and the rate of sedimentation, etc., are high; these behaviours are discussed in the appropriate section.

The suspensions were prepared by triturating a sample of lamp-black (B.D.H.) or material to B.S. specification 284, with the oil in a pestle and mortar, and allowing the mixture to stand for a few days to allow of thorough wetting; carbon black can adsorb up to about 10 per cent. gases (Rossman and Smith [19]).

I. The Specific Viscosity of Suspensions of Carbon Black.

The specific viscosity can be expressed as $\frac{\eta - \eta_0}{\eta_0}$ or $\eta/\eta_0 - 1$, where η is the viscosity of the suspension, η_0 that of the liquid; η/η_0 is known as the relative viscosity.

As already mentioned, the viscosity of carbon black and other micro-particles suspended in liquids being greatly affected by flocculation, it is possible to obtain some idea of the degree of flocculation from viscosity measurements and comparing the slope of the curves relating specific viscosity with concentration in volume.

The high viscosity of flocculated suspensions is due (*a*) to a part of the energy normally used to cause flow being diverted to the breaking up of the three dimensional structure and deflocculation (thixotropy effect), (*b*) to liquid being held within the flocks, so decreasing the proportion of suspending medium and increasing the volume of dispersed material, and (*c*) to energy being required to cause orientation of the flocks and of anisodimensional particles during their precessional movements in the stream of flow.

The curve relating the specific viscosity of the carbon-black suspensions with concentration in volume per cent. is practically straight up to about 1 per cent., and subsequently a curvature develops. The slope of the curve was found to vary from about 5 to 12·5 times the volume of carbon black per c.c. of suspension; Einstein calculated a value of 2·5 for an ideal suspension of spheres without interaction. The highest coefficients were obtained with flocculated suspensions in paraffin hydrocarbons, while in castor oil, in which flocculation was least apparent, a low reading was obtained. The method of experiment for determining the specific viscosity of the carbon suspensions was practically the same as already described, and measurements were made with the apparatus shown in Fig. 1, using suction when required. The rate of shear was kept as constant as possible for the suspensions in the various oils and organic media of widely different viscosity. Capillary tubes of bore less than 1 mm. were avoided because of the danger of partial chokage with resulting high coefficients; the viscometers were frequently calibrated with the pure suspending medium because of depositions on the walls.

The viscosity coefficients for lamp-black in various liquids at 20° C. are shown in Table IV, Fig. 8, from which it will be seen that fairly big differences in specific viscosity can be reported.

FIG. 8. THE SPECIFIC VISCOSITY OF CARBON BLACK SUSPENSIONS IN OILS.

TABLE IV.

The Specific Viscosity of Carbon Suspensions in Various Liquids at 20° C.

Suspending Liquid.	Viscosity Coefficient.
Ideal suspension (Einstein)	2·5
Castor oil, B.P.	5·3
Russian mineral oil, sp. gr. 0·896	7·8
Aero-engine oil	9·5
Oleic acid	9·8
Carbon tetrachloride	10·0
Toluene	11·0
White spirit	11·6
Liquid paraffinum, sp. gr. 0·84	12·3

Newtonian Character of Suspensions in Viscous Liquids.

It was found in previous work [20] that the specific viscosity of suspensions and colloidal sols is greater the greater the viscosity of the suspending medium. This behaviour appears to be explicable on the assumption that in the more viscous liquids the flocks and anisodimensional particles take longer to orientate in the stream of flow, and so cause eddying over a longer period of time and to a greater extent. Because of this behaviour, the relative coefficients—say 5·3 for castor oil, viscosity 10 poises, and 11·0 for toluene, viscosity 0·0058 poises—become more divergent when corrected to unit viscosity, the coefficient for castor oil decreasing and that for toluene increasing. The marked influence of the viscosity of the medium on the specific viscosity of suspensions is shown in the following data (*a*) for bentonite in paraffin hydrocarbons and (*b*) for ultramarine in raw linseed oil, conc. 12 per cent. volume given in Table V. Mardles (*loc. cit.*).

TABLE V.

The Variation of Specific Viscosity with Viscosity of the Medium.

(*a*) Bentonite in Paraffin Hydrocarbons.

Viscosity of medium in centipoises	0·3	0·6	1·5	4·6
Viscosity coefficients	7·5	9·3	10·7	12·0

(*b*) Ultramarine in Raw Linseed Oil.

Viscosity of medium in centipoises	8·9	10·5	17·6	23·5	33
Specific viscosity	1·2	1·3	2·1	2·3	2·4

The important part played by the viscosity of the medium on the behaviour of the suspension is shown by the fact that carbon suspensions in the more viscous liquids appear to be more Newtonian in character than carbon suspensions in liquids of low viscosity; with the latter a definite and relatively large yield value can be measured. Some results illustrating this behaviour are shown in Fig. 9 A and B; results shown in Fig. 9 A were obtained with the Stormer type of viscometer, and in Fig. 9 B by tackmeter measurements where two surfaces with the suspension between were separated by a pull normal to the surface. In the tackmeter a circular metal flat of stainless steel, 3 cm. in diameter, was suspended from one end of a balance beam; a distance between the surface of the metal disc and surface of a glass flat was kept by means of

A. Stormer. B. Tackmeter. 0·2

A. Stormer.

B. Tackmeter.

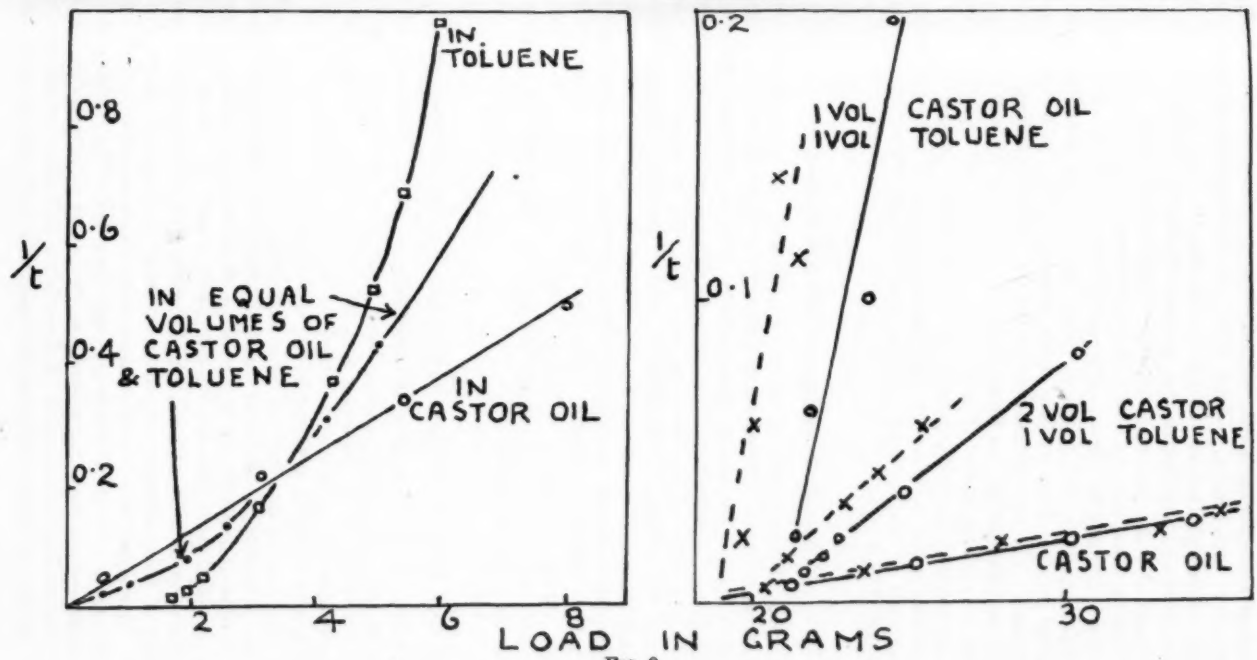


FIG. 9.

FLOW BEHAVIOUR OF CARBON BLACK SUSPENSIONS, 7 GM./100 C.C. IN CASTOR OIL AND TOLUENE AND THEIR MIXTURES.

—O—O—O— Suspension.

--X--X--X-- Medium alone.

two wires 0·0024-inch diameter, and a volume of 0·2 c.c. was used between the surfaces. The time in seconds taken for one complete revolution of the viscometer cylinder, or the time taken for the disc to break away with known loads, was noted, and the curves relating $1/t$, the reciprocal of the time, and the load were plotted. With carbon black in castor oil the viscosity behaviour was Newtonian, the curve passing through the origin and remaining rectilinear as far as the tests went; in the tackmeter both liquid medium and the suspension gave almost identical results, indicating freedom from rigidity shown by suspensions in toluene–castor oil mixtures. The carbon-black suspension in toluene possessed a definite yield value indicated by the Stormer-type viscometer, while a suspension in equal volumes of castor oil and toluene, although not showing a yield value, gave a curvilinear relationship indicative of flocculation.

In the tackmeter a yield value was indicated equivalent to the amount of separation of the curves for liquid medium (chain line) and for the suspension (Fig. 9 B).

Specific Viscosity and Sediment Volume.

The value of the specific viscosity of suspensions can be correlated with the sediment volume. Ostwald and Haller,[21] working with micro-powders in single liquids, have shown that particles of talc, graphite, bentonite, etc., which are flocculated in carbon tetrachloride assume a higher sediment volume and possess higher viscosity than in alcohol in which a large proportion of the powder is dispersed as single particles. Buságh [22] also concluded that with micro-powders the higher the degree of flocculation the greater the sediment volume, while Winkler [23] has measured thixotropy in terms of sediment volume. Mardles [24] has reported a correlation between specific viscosity, sediment volume, and yield point. Data illustrating this behaviour are given later in the paper for various suspensions of carbon black.

II. The Rate of Sedimentation and Volume of Sediment.

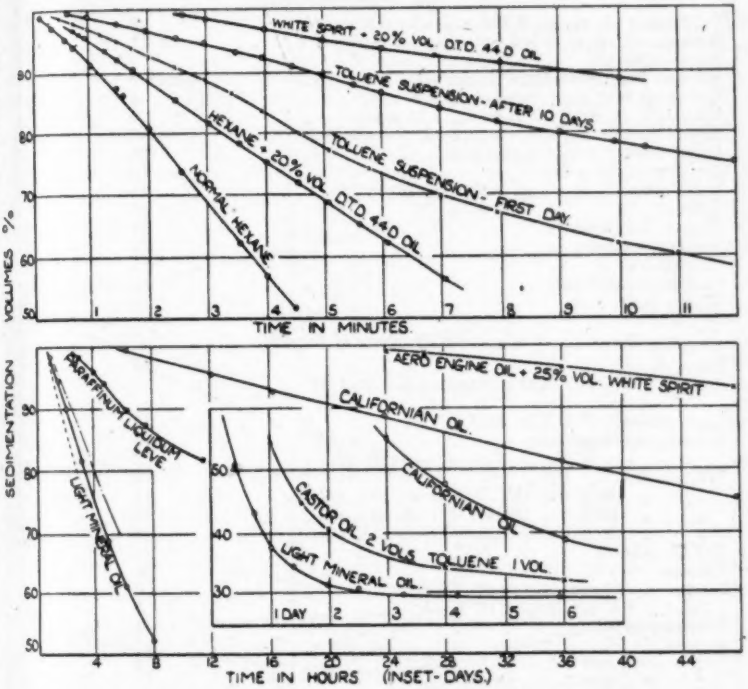
Measurements of the rate of sedimentation of carbon black suspended in various oils and organic liquids were made in glass tubes of various sizes up to about 3 cm. diameter and 50 cm. in length; for comparing sediment volumes in mixtures test-tubes of size 1 cm. diameter and 25 cm. in length were found to be suitable.

The procedure of test was the same as described by other workers, and as in the sedimentation of blood corpuscles using the Westergren type of tube, Gordon and Wardley,[25] the position of the sharp separation of the sediment layer from the clear liquid being noted from time to time. Figures, as shown in Fig. 10, relating the sediment volume with time were prepared, and the sediment rate reckoned from the maximum slope of the curve. The ultimate sediment volumes were measured after several days or weeks, when little or no further change occurred. The freshly-shaken suspensions did not clear immediately at the top on sedimentation, but a period of time elapsed during which flocculation and some turbulence due to the settling of coarser particles occurred; a steady rate of sedimenta-

tion for a time, then the rate gradually decreased until a constant volume of sediment was obtained.

The relationship between time and the sediment volume is shown in Fig. 10 for a few liquids, the rate of sedimentation was obtained during the period when the settling appeared to be steady and was actually measured from the maximum slope of the curve.

Naturally, in the more viscous and denser oils the sedimentation is


WHITE SPIRIT + 20% VOL. DTD 44.D OIL
TOLUENE SUSPENSION - AFTER 10 DAYS.
HEXANE + 20% VOL. DTD 44.D OIL
TOLUENE SUSPENSION - FIRST DAY
NORMAL HEXANE
VOLUMES %
TIME IN MINUTES.
AERO ENGINE OIL + 25% VOL. WHITE SPIRIT
CALIFORNIAN OIL.
PARAFFINUM LIQUIDUM LEVE
LIGHT MINERAL OIL
CASTOR OIL 2 VOLS. TOLUENE 1 VOL.
SEDIMENTATION
TIME IN HOURS (INSET - DAYS.)

— — — — For conc. 1gr./100 c.c. — o — o — With addition of 0·1% of water.

FIG. 10.

RATES OF SEDIMENTATION OF CARBON BLACK.

slower (*a*) in proportion to the viscosity of the oil and (*b*) inversely to the density difference between the carbon and the oil, according to the well-known Stokes law; the sedimentation rates of carbon black in various liquids have been reckoned for unit viscosity and unit difference in density.

Some experimental results for the sedimentation rates of carbon black in various oils, hydrocarbons, and their mixtures are given in the following Table VI.

The sedimentation rates corrected for viscosity and density (the density of the carbon black was taken as 1·77) difference of carbon black in the various oils and mixtures were determined at 20° C. using tubes of 1·5 cm.

TABLE VI.

The Sedimentation Rates at 20° C. of: (a) *A Sample of Carbon Black (B.D.H.) in Various Mineral Oils, Hydrocarbons, etc.;* (b) *In their Mixtures.*

Description of Suspending Medium.	Sedimentation Rate in cms./sec. × Viscosity of Medium ÷ Density Difference, × 10^5.
(a) *Single Liquids.*	
Californian oil, sp. gr. 0·929, viscosity 0·62 poises	3
Russian oil, sp. gr. 0·905, viscosity 1·3 poises	11
Aero-engine oil	3·5
Filtered Pennsylvanian cylinder oil	about 1
Castor oil B.P. (carbon black, B.S.S. 284)	3
Texan oil, sp. gr. 0·94, viscosity 4·44 poises	9
Liquid paraffinum, leve, sp. gr. 0·83, viscosity 0·25	15
Ditto, freshly prepared suspension	38
Ditto, after 24 hours	19
Light mineral oil, sp. gr. 0·83, viscosity 0·18	22
Toluene	20
Xylene, technical	23
Normal hexane	29
Chloroform	19
Carbon tetrachloride	20
White spirit	19
(b) *Mixtures of Liquids.*	
Hexane	29
„ + 7% vol. light mineral oil D.T.D. 44D.	28
„ + 20% „ „ „ „	17
Light mineral oil D.T.D. 44D	15
Liquid paraffinum leve	15
„ „ „ + 33% aero-engine oil	2
White spirit	19
„ „ 80% vol. D.T.D. 44D oil, 20% vol..	11
„ „ 60% vol. D.T.D. 44D oil, 40% vol..	10
„ „ 25% vol. D.T.D. 44D oil, 75% vol..	13
D.T.D. 44D oil	15
Toluene	20
„ 1 vol. aero-engine oil 3 vols.	6
„ 1 vol. aero-engine oil 4 vols.	4
Aero-engine oil	3·5
Xylene	23
„ 99% vol. Texan oil 1% vol.	22
„ 98% vol. Texan oil 2% vol.	21
„ 95% vol. Texan oil 5% vol.	19
„ 90% vol. Texan oil 10% vol.	16
„ 80% vol. Texan oil 20% vol.	7
„ 30% vol. Texan oil 70% vol.	8
Texan oil	9
Toluene (2nd sample carbon black, B.S.S. 284)	7·2
„ 2 vol. castor oil 1 vol.	6·0
„ 1 vol. castor oil 1 vol.	5·0
„ 2 vol. castor oil 3 vol.	5·5
„ 1 vol. castor oil 4 vol.	6·0
„ 1 vol. castor oil 9 vol.	6·3
Castor oil	6·3

diameter, the height of the suspension being kept at 40 cm.; the concentration of the carbon black was 5 gr./100 c.c.

The sedimentation rates are comparative and approximate, it being known that the rates are dependent to some extent on the concentration

of the suspension and on the height of the suspension, as well as on the time after shaking. The results are sufficiently diverse to indicate big differences in the degree of dispersion, and it is interesting to note that there is (*a*) a correlation between the specific viscosity and sedimentation rate in as far as where the specific viscosity is below 10 the sedimentation rates are considerably smaller than when the specific viscosity is above

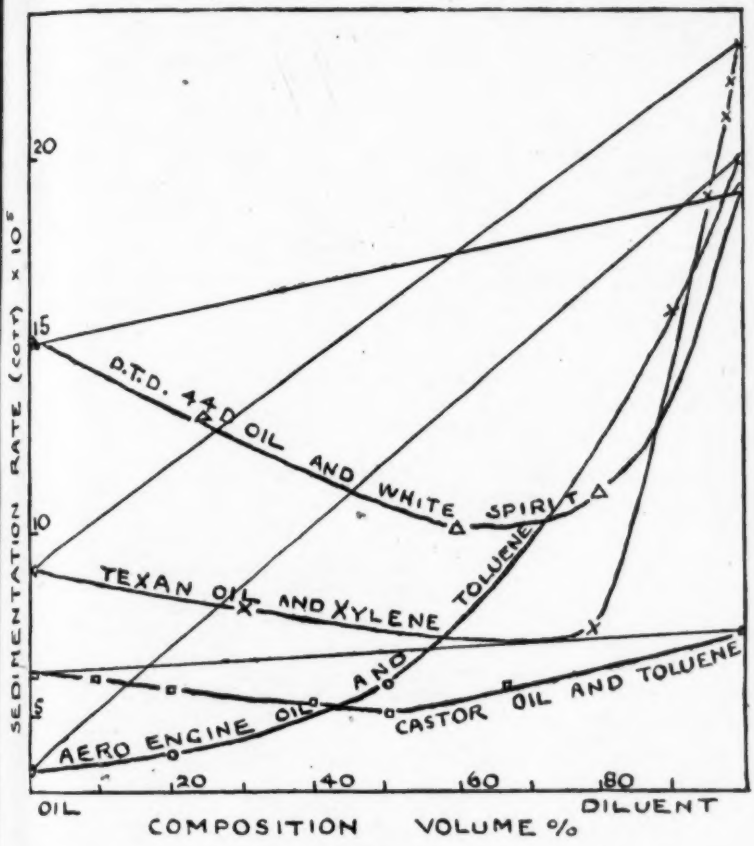


FIG. 11.

SEDIMENTATION RATES OF CARBON BLACK IN DILUTED OILS.

10, and (*b*) that in mixtures the sediment rate is less than the calculated average, Fig. 1. Table VII gives results for specific viscosity and sedimentation rates for six liquids.

With regard to the correlation between specific viscosity and sedimentation rate, further work is required; it is possible that the sedimentation rate is affected by the slight rigidity of the oils, and this is being investigated. Larsen and Talley (*loc. cit.*) found with regard to carbon-

TABLE VII.

Specific Viscosity and Sedimentation Rates.

Liquid.	Specific Viscosity.	Sedimentation Rate (corr.).
Castor oil	5·3	3
Aero engine	9·5	3·5
Carbon tetrachloride	10·5	20
Toluene	11	20
White spirit	11·6	19
Liquid paraffinum	12·3	25

black suspensions in oils that there was no correlation of the detergency rating by rate of settling and general engine experience. They found, for example, that some effective detergents were rated poor and a few plain oils without detergent additions were rated excellently.

Flocculation and Sediment Volume.

With a high degree of flocculation, such as occurs with a bentonite clay in water suspension, a small quantity of material, say 2 gr./100 c.c., occupies practically the whole volume of the suspension, while in another liquid, such as alcohol, when flocculation is not high the volume occupied by the sediment is about the same as the powder occupies in the dry state. As already stated, various workers have used the value of the sediment volume as a measure of the degree of flocculation and also of thixotropy.

Some sediment values for carbon black in various liquids and their mixtures are given in Table VIII and Figs. 12 and 13. The sediment

TABLE VIII.

Specific Sediment Volume of Carbon Black in Various Liquids at 20° C.

Liquid.	Volume, c.cs.	
	1 c.c. Carbon Black.	1 gm. of Graphite (Ostwald and Haller).
Carbon tetrachloride	15·2	2·7
Chloroform	12·2	2·2
Normal hexane	11·9	2·5
White spirit	12·4	—
Paraffin oil	12·5	—
*cyclo*Hexane	10·9	2·55
Benzene	11·6	2·43
Toluene	11·3	2·40
Xylene	10·9	—
Ethyl alcohol	9·2	1·75
Acetone	9·2	1·7
Aniline	11·8	1·8
Dekalin	10·9	—
Tetralin	10·4	—
Linseed oil	10·4	—
Texan mineral lubricating oil, sp. gr. 0·94	10·4	—
Russian lubricating oil, sp. gr. 0·896	10·9	—
Light mineral oil, D.T.D. 44D	12·2	—
Aero-engine oil	10·2	—

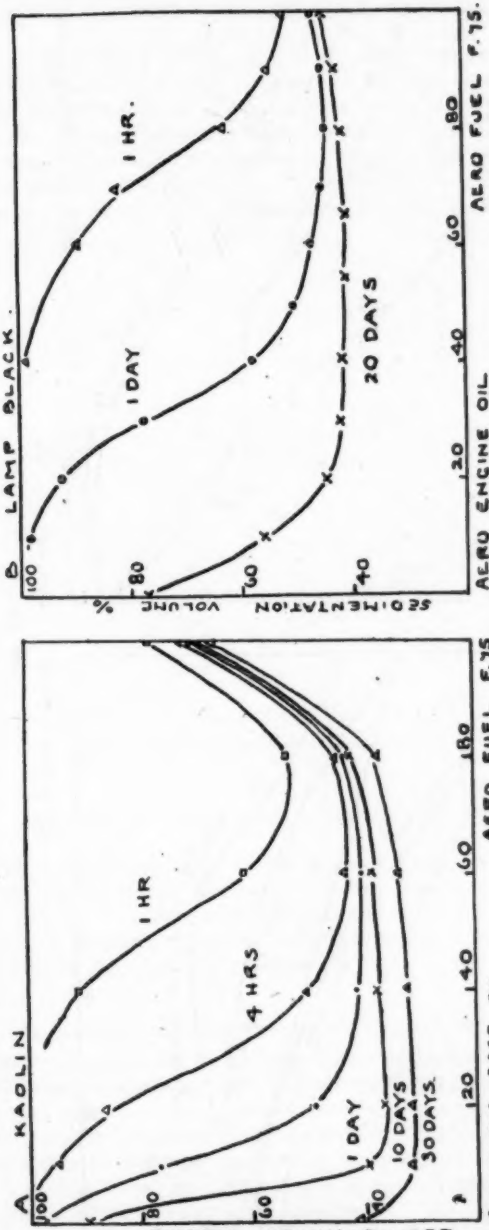


FIG. 12.

THE SEDIMENTATION OF MICRO PARTICLES IN DILUTED LUBRICATING OILS.

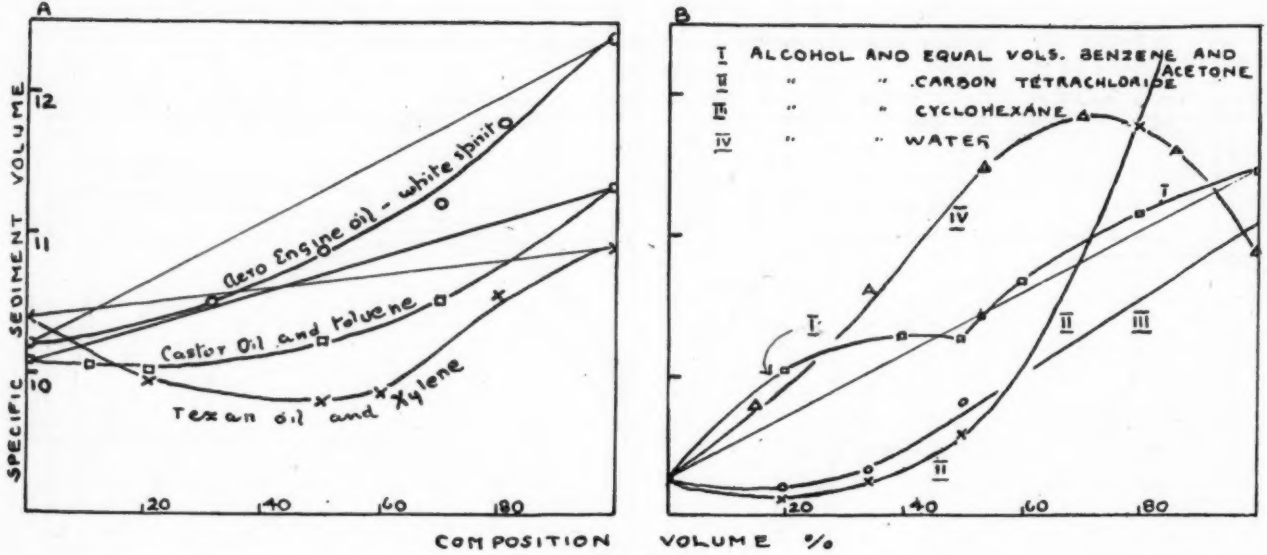


FIG. 13.

THE SPECIFIC SEDIMENT VOLUME OF CARBON BLACK IN (A) DILUTED LUBRICATION OILS AND (B) BINARY MIXTURES OF ALCOHOLS.

volume has been expressed as the volume occupied by 1 c.c. of the material.

From the above list it will be seen that carbon tetrachloride, hydrocarbons, and other "non-polar" liquids yield high specific sediment volumes for the carbon-black suspensions; a similar behaviour has been found by Ostwald and Haller and other workers using graphite and other micro-particles. That there is a correlation between the specific sediment volume and the rate of sedimentation, corrected for viscosity and density differences, can be seen by comparing data in Figs. 11, 12, and 13.

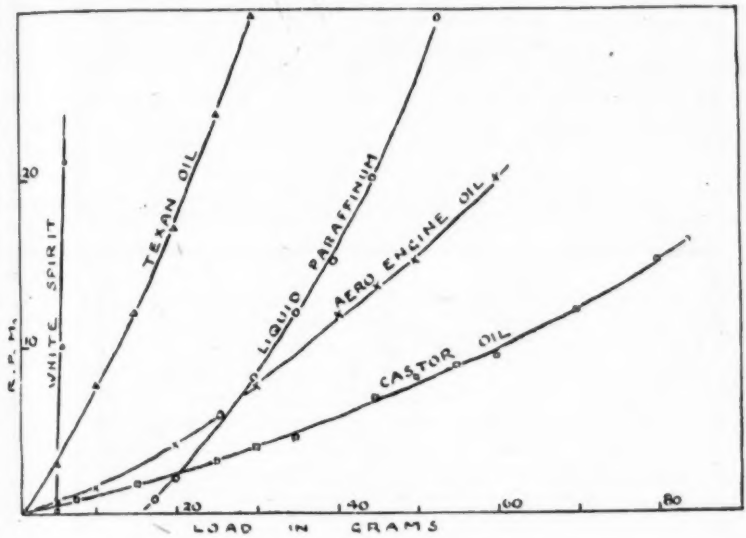


FIG. 14.

VISCOSITY OF CARBON BLACK SUSPENSIONS—STORMER.

Although specific sediment volumes below the average value for mixtures were obtained with diluted oils, values above the average were obtained with carbon black in binary mixtures of alcohol and water (Fig. 13 B), while in mixtures of alcohol with benzene and acetone values both above and below the average were obtained.

III. The Rigidity of Suspensions of Carbon Black in Oils.

The rigidity of suspensions in various oils due to the flocculation of carbon black has been measured by balancing the rigidity against the torsion of a fine metal wire, a method already used by other workers—McDowell and Usher (*loc. cit.*), Hobson.[27] The wire was 150 cm. long, of diameter either 0·0024 inch, 0·004 inch, or 0·0108 inch, according to the concentration of carbon black, and from it was suspended centrally the hollow cylinder of a Stormer viscometer immersed in the suspension with a clearance of 4 mm. from the sides of the containing vessel. The method

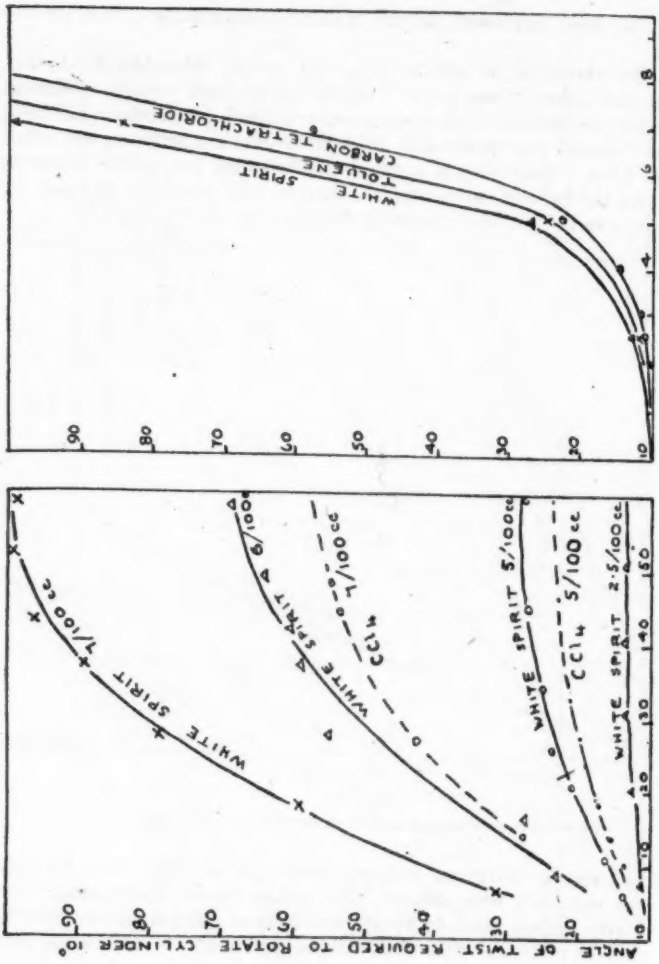


FIG. 15.
THE RIGIDITY OF CARBON BLACK SUSPENSIONS.

of experiment was to determine the angle through which the top end of the wire had to be rotated in order to give a movement of 10° at the bottom end. As other workers have found, it was necessary to protect the apparatus from draughts and to rotate the top end of the wire slowly and without jerks; usually the top end was rotated through an angle of 90° and the angle of twist noted when the cylinder had come to rest. The rigidity results by the torsion method have been amplified by viscosity results with the same suspensions in the Stormer viscometer. These latter results, which are shown in Fig. 14, indicate clearly the differences in the degree of flocculation of the carbon black in the various media,

and link up with the rigidity results and measurements of sediment volume, etc.

It will be seen that, in the Stormer type of viscometer used, with both white spirit and liquid paraffinum the carbon-black concentration 20 gm./100 c.c. has a well-defined yield value of 5 and 15 gm. respectively; on the other hand, with castor oil, aero-engine oil, and Texan oil the curves pass through the origin in keeping with their relatively low specific viscosity and low rate of sedimentation.

In the torsion experiments the rigidity was measured after different intervals of time, after well stirring the suspensions; few readings as possible were taken, as each twist tends to destroy the fragile structure. After standing for some time the rigidity measurements seem to reach a maximum and then, on further standing, tend to fall. Some results for different concentrations of carbon black in white spirit and carbon tetrachloride respectively are shown in Fig. 15 A. The ordinate is the angle of rotation required to produce a movement of 10° of the cylinder in the suspension. In Fig. 15 B results are shown relating the rigidity with the concentration; the structural rigidity appears to vary between the third and fourth power of the concentration. Phillipoff and Hess,[28] working with trinitro-cotton in butyl acetate, found a value of the eighth power for the structure.

When white spirit was mixed with a little engine oil, the rigidity of the white spirit suspensions decreased appreciably; thus, with the addition of 10 per cent. volume aero-engine oil the rigidity was reduced to about a half of the original value of the white spirit. This is in accord with other findings of reduced flocculation. With mixtures of castor oil and toluene using a concentration of 7 gm./100 c.c. there was little rigidity manifested until at least the greater part of the mixture was toluene.

With concentrations of carbon black of 20 gm./100 c.c. and higher in castor and other oils possessing good dispersing action, evidence of flocculation can be obtained by the torsion method; some results are shown in Table IX for higher concentrations with a wire of diameter 0·0108 inch.

TABLE IX.

Relative Rigidity of Carbon-black Suspensions.

Substance.	Angle of Rotation required to Turn Cylinder 10°.	
	Conc. 15 gm./100 c.c.	Conc. 20 gm./100 c.c.
Aero-engine oil	10·3	12
Castor oil, B.P.	10·2	11·4
Paraffinum liquidum, leve . .	—	31·3
D.T.D. 44D oil	18	35·0
White spirit	—	Above 50

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LUBRICATING GREASES.

By A. S. C. Lawrence, Ph.D., F.R.I.C., F.Inst.Pet.

Greases are mixtures of a small number of soaps dispersed in mixtures of hydrocarbons. Their use depends in all cases on their special rheological properties, yet little has been done to study these or to control them except by rule-of-thumb methods. The well-known work of Arveson and of Blott and Samuel forms a valuable contribution to our knowledge of their rheology, but there is no reason to suppose that study of their lubricating and flow properties at very high rates of shear under heavy loads would not be of great value. Methods of preparation of greases still too closely resemble cookery-book stuff, and no serious attempt seems to have been made to assess the influence of the quite small number of components and their permutations. This applies both to soaps and also to the oil-dispersion medium. The latter factor is almost certainly much less important. No serious attention has been given to the rôle of small amounts of polar impurities, such as water and glycerin, which may profoundly modify the resulting grease and, indeed, in the case of the lime-soap greases, water is an essential component. This state of affairs is undoubtedly due to the fact that grease is usually used for low-grade lubrication, by which is meant that almost any lubricant would do the job well enough. It is chosen in preference to oil only because grease acts as a dirt-excluding seal. Also, grease-cups use the consistency of the grease in place of a mechanical means of supplying oil in small amounts over a long period. The total production of greases is small compared with that of lubricating oils, but a better understanding of greases would benefit manufacturers, if only by enabling them to reduce the number of types made and to convince the users that they are being offered something better than that used by their grandfather.

The Nature of Soap/Oil Dispersions.

Soaps are very peculiar substances. One of their still unexplained properties is that, with oil, they form greases. I cannot say why they do, but I am going to try to describe what sort of systems greases are, as the first step towards answering that question. The colloid chemistry of aqueous soap solutions has been studied very thoroughly; first, by the classical work of McBain, and, recently, expanded and reinterpreted especially by Bury and Hartley [1] in this country. The revival of interest was stimulated by the appearance on the market of the new synthetic detergents and wetting agents. The carboxylic acid salt soaps still, however, present some special features which have not yet been explained. I do not believe that pure anhydrous sodium soaps of the fatty acids have ever been prepared, although extensive observations have been made on allegedly pure sodium palmitate and stearate.[2] The analytical data necessary to decide whether these soaps were really anhydrous is lacking, and later X-ray data are so mutually contradictory and unsatisfactory

that a decision cannot be reached.[2] The number of phases through which these soaps can pass on heating is obviously of the greatest importance in dealing with soda-soap greases, and the great influence of small amounts of water makes it very desirable that this matter should be cleared up as a practical point as well as one of great academic interest.

Shortly before the War, work was carried out by the writer and by G. S. Hartley on two additional peculiarities of aqueous soap solutions: peptization by small amounts of polar substances;[3] and internal solubility of oil-soluble substances in the interior of the soap micelle in water.[4] I was also able to show that peptization occurred in oil dispersions of soaps in a manner closely parallel with that in aqueous systems.[5] I shall refer to these properties in more detail later.

Phase Changes in Soaps.

Many soaps, when heated in an oil of sufficiently high boiling point, form a fluid solution when hot, which sets to a clear gel on cooling to a Temperature T_1. At some lower temperature T_2, it becomes opaque, and can be shown by suitable methods to be a suspension of micro-crystals of the soap. When heated alone, the soaps melt at a high temperature to normal liquid. On cooling, this passes at T_1 to a plastic or resinous state which continues to increase in viscosity as it cools further. At the lower temperature, T_2, it undergoes a sharp transition to a micro-crystalline solid. At this change the viscosity of the plastic phase is very great—of the order of that of pitch—and the crystals formed are very minute, and often not resolvable under the microscope. However, there is no doubt about the transition. Above it the plastic phase adheres to glass, whereas below it there is no adhesion. The plastic phase gives only side spacings when examined by X-rays, but the brittle solid gives the normal long spacings. In many cases, too, threads can be drawn out of the plastic phase, and if this is done as the transition is occurring, the crystallites are orientated as they grow and a fibre is formed with high birefringence and parallel extinction. No optical evidence of orientation in the plastic phase has been found even in the aluminium soaps, which are peculiar in showing macroscopic elasticity. It is therefore concluded that these soaps exist in the three phases: isotropic liquid (usually above 200° C.), plastic or resinous, fully crystalline solid. In solution, in oil, the corresponding phases are: isotropic fluid, clear elastic gel, and suspension of micro-crystals. The consistency is greatest in the gel phase, so that we can expect that a grease shall lose consistency at low temperature and on heating become suddenly more viscous. This applies, of course, to a grease made from a single soap and a single hydrocarbon as oil. Actually the latter criterion is not so serious, and such sharp transitions have been observed using Nujol as oil. Aluminium monostearate then shows the phenomena described very well. The separation of the micro-crystalline soap is, however, delayed considerably, and the mixture may remain metastable for some days. When the soap has separated, the sudden increase in viscosity on warming to the gelation transition is very marked. The metastability increases with increase of concentration of soap, and, at the concentrations used in commercial

greases, the micro-crystalline phase becomes a paste rather than a suspension, and will show rigidity if the crystals lock together. In this way the fall of consistency at this transition point may be masked. I suggest that no difference should be found between worked and unworked consistencies for greases in the gel state, and that such differences, when found, are indication that part or all of the soap is crystalline. A simple method was found for determination of the phase of a specimen of high consistency. It is mixed with an excess of Nujol, and then passed through a homogenizer (of the domestic cream-making type). The diluted mixture

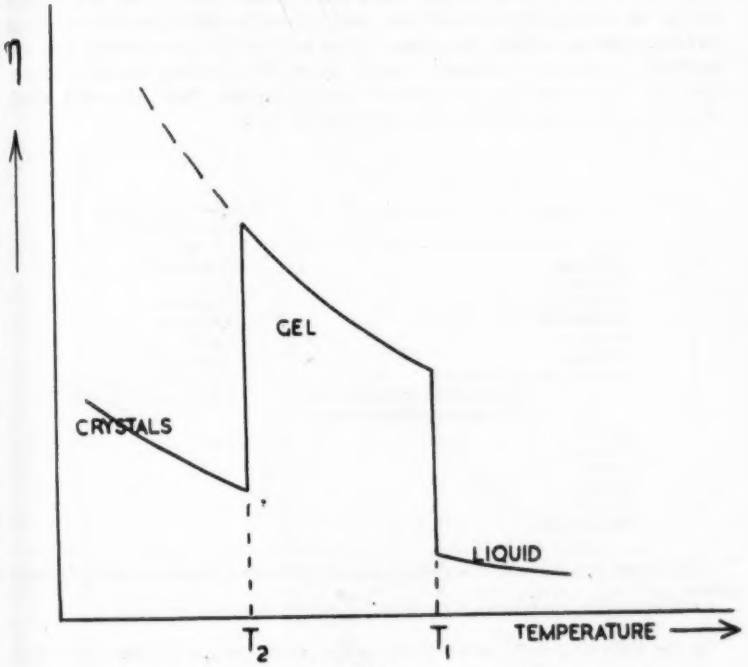

FIG. 1.

is illuminated by a concentrated beam of light. If in the gel phase, it is optically empty. If below its T_2, a bright Tyndall cone will be seen. With mixtures of soaps present, part may be gel and part micro-crystalline. Fig. 1 shows the viscosity–temperature changes diagrammatically. The broken line is the metastable region.

EFFECT OF COMPONENTS ON PROPERTIES OF GREASES.

We may now list the variables which determine the properties of a grease. The nature of the oil is less important, and very little is known of the relation of its chemical composition to solvent power for soaps. It is well known, of course, that the consistency of a grease can be controlled

to a considerable extent by variation of the viscosity of the oil. The other variables are: nature of metal, nature of fatty acid—its molecular weight, effect of unsaturation, structure if not straight chain, presence of peptizing substances—water and fatty acid, effect of mixing fatty acids with common metal, effect of mixing metal soaps of a common acid, effect of mixing soaps in which both metal and fatty acid are different.

Table I shows the effect of the metal part of the soap. (For a fuller list with values of T_1 and T_2 for soaps and soap–oil systems, see A. S. C. Lawrence, *Trans. Faraday Soc.*, 1938, **34**, 660.) Those which do not form gel have lower melting points than those which do. They are usually soluble in all organic solvents hot, and crystallize like the fatty acids on cooling. Those which do gelate have higher melting points and are insoluble in organic solvents, except those with boiling points above *c.* 150° C. Some can be crystallized from pyridine, but the solid which separates on cooling is slimy and difficult to filter.

TABLE I.

Metals whose Soaps Gelate.	Metals whose Soaps do not Gelate.
Lithium	Ammonium
Sodium	Zinc
Potassium	Mercury
Rubidium	Thorium
Barium	Lead
Calcium	Thallous *
Aluminium (tristearate)	Beryllium †
,, (monohydroxy distearate)	Ferric
,, (dihydroxy monostearate)	
Silver	
Nickel	
Cobalt	
Copper	
Uranyl	
Magnesium	

* The thallous soaps are dimorphous, passing through a liquid crystalline smectic phase.

† Co-ordination compounds, sometimes incorrectly described as basic.

In the following sections only the gelling metal soaps will be considered.

The Effect of the Fatty Acid.

The metal soaps begin to become soluble in hot oil at a fatty acid chain length of C_{12} Lauric acid. There is a rapid change in solubility over the short range of the commercially available acids from lauric to stearic. The laurates are usually soluble only at very high temperatures—of the order of 300° C. Fig. 2 shows the phase changes for the soda soaps alone and in Nujol. The laurate dissolves in boiling Nujol, but separates on cooling as a liquid, which appears to be the soap swollen with oil. On cooling, the transition to crystalline soap occurs, but there is no true gel phase. This appears in the myristate. The lithium soaps show a similar rapid change of properties over a difference of a few carbon atoms chain length. The laurate is soluble hot, but no gel phase intervenes.

Fig. 2 shows clearly that the "solubility" of soaps in oil is mainly due to thermal loosening of bonds, so that solubility to true solution is an abrupt change occurring over a few degrees at most. There is some

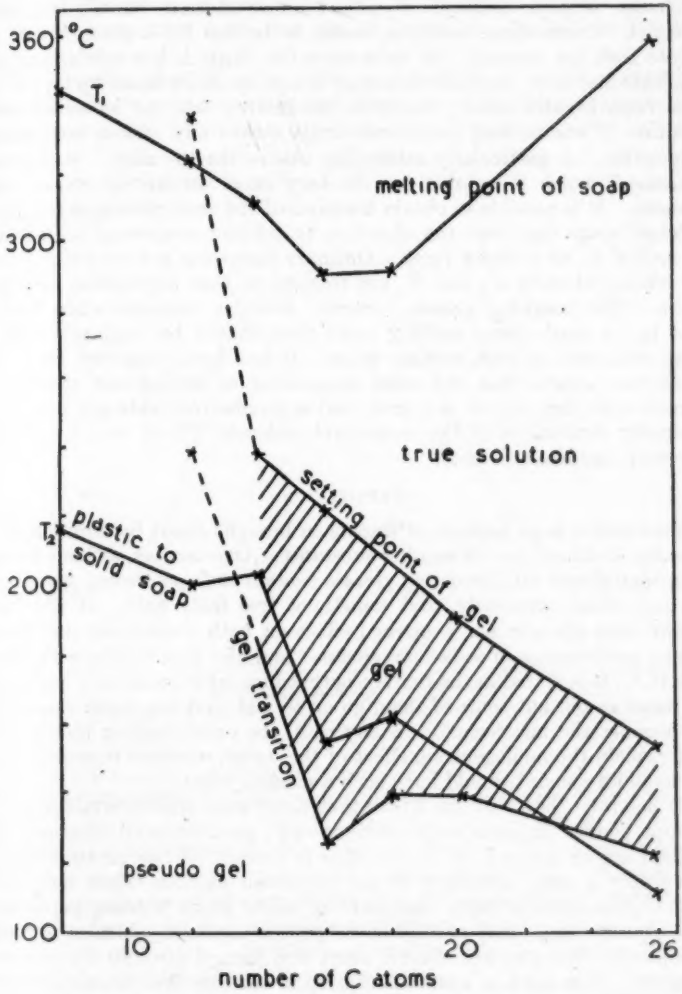

FIG. 2.

indication, in the cases of calcium stearate and sodium laurate studied, that at T_1 in oil the very marked expansion which occurs takes place over a degree or two, but more accurate work is required to show whether the very poor thermal conductivity of the systems is responsible for this

spread and whether it is a really sharp transition. The difference between the melting point of sodium cerotate and its T_1 in Nujol suggests that, with this length of hydrocarbon chain, a real solvent action is appearing.

The effect of the double bond, as shown by comparison of oleates with stearates, is quite definite. T_1 is not much affected, but T_2 is greatly lowered. Consistency, however, seems to be less for a given weight of oleate than for stearate. In some cases the oleate is less soluble and the linoleate still less. Sodium stearolate is also insoluble in oil up to 340° C. The naphthenates closely resemble the oleates, but the indefinite composition of commercial naphthenic acids makes any serious comparison impossible. A particularly interesting case is the so-called "wool-grease stearine," which is notable for the very small amount of stearic acid present. It is possible to obtain fractions of the acids present which form calcium soaps free from the objection to calcium stearate of segregating at *c.* 119° C. as a sticky lump. Ordinary lime-soap greases are peptized by water, whereby T_1 and T_2 are reduced so that segregation does not occur. The resulting grease, however, becomes unstable when heated and has a much lower melting point than should be attainable with a soap with such a high melting point. It has been suggested from the molecular weight that the chief component of wool-grease stearine is cerotic acid, but this is not true, and a number of acids are present—probably derivatives of the cholesterol molecule. They would resemble the soap-like bile acid salts.

Peptization.

Peptization is an increase of dispersion brought about by addition of a, usually, small amount of another substance. One can say without hesitation that almost all lubricating greases contain such peptizers; water and glycerin most commonly, and sometimes free fatty acid. It has been shown that glycerin has a marked effect on both consistency and lubricating performance of soda-soap greases [6] and also that it affects the fibre length.[7] It is stated in the textbooks that lime-soap greases are emulsions of water in oil, but some of them go on to add that the water cannot be seen under the microscope. In any case, the emulsification theory does not explain the homogenizing effect of the water, nor does it explain why so small an amount should have such a marked effect.

It has been shown by the writer that many substances containing polar groups peptize aqueous soap solutions—*e.g.*, phenols, acids, alcohols, and amines are all active.[3] It is a further criterion that the peptizer should have only a small solubility in the dispersion medium, since there is a distribution ratio between that and the solute which is being peptized—*e.g.*, glycerin and ethyl alcohol never peptize aqueous solutions of soaps completely, but the less soluble amyl and benzyl alcohols do in small amount. Non-aqueous solutions of soap in solvents such as ethyl alcohol are peptized by water. It was then shown that dispersions of soap in oil are also peptized by the same substances.[5] Their effect is simply to lower the values of T_1 and T_2. These fall steeply at first, then more slowly, and finally become asymptotic at the setting point of the mixture. At this stage the soap separates separately, and the peptizer, if liquid and sufficiently soluble, remains in solution in the oil. The writer has shown

that any fatty acid from acetic upwards can peptize sodium and calcium stearates, provided that the equimolecular ratio is not exceeded. If it is exceeded, the stronger acid—*e.g.*, acetic—will decompose the stearate. In the peptization there is no exchange of fatty radicles between soap and peptizer. Complexes of soap and fatty acid peptizer have been prepared in the equimolecular ratio and are characterized by definite melting points.[5]

Now consider what happens when a peptizer is added to a soap–oil dispersion, the temperature being kept constant. Fig. 3 shows the changes of consistency. If the peptizer is added to the paste phase, great increase

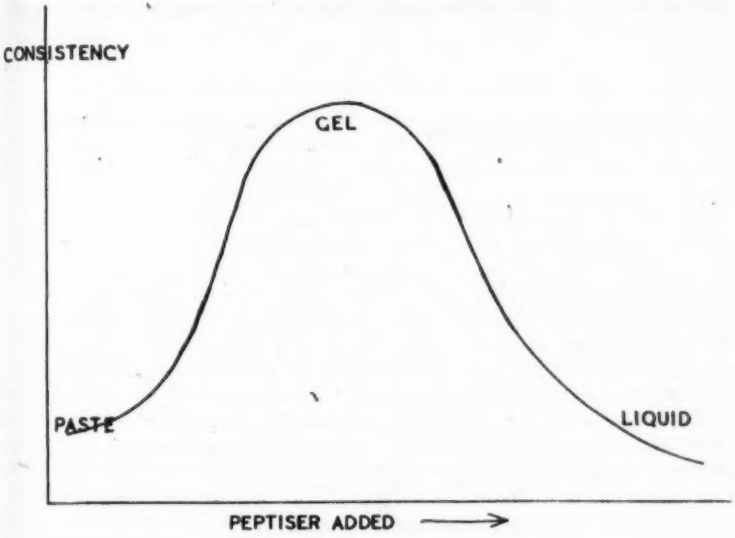

FIG. 3.

of body will result, but if the mixture is already in the gel phase, consistency will be reduced. This curve is strikingly similar to that given by heating. This is shown in Fig. 1. Here the changes will be abrupt at the transition temperatures for a single pure soap. Both these types of curve are shown completely by aluminium monostearate, but with the further complication that, on cooling, the gel phase remains metastable for some days, and its consistency therefore follows the dotted line immediately on cooling. On standing for long enough, it falls to the full line, and then follows the full line on re-heating.

Mixtures are more efficient as peptizers than their components singly—*e.g.*, cresol and oleic acid or amyl alcohol and oleic acid added to sodium stearate. Fig. 4 shows the phase diagram for a 2 per cent. solution of soap. There is some uncertainty about the boundary between suspension and solution when excess of peptizer was added, but that part of the system was not examined. As already mentioned, the absolute sharpness of the

solution–gel transformation is not established, but there is no difficulty in observing it with sufficient accuracy for the construction of the phase diagram.

As a guide, one may say that the extent of lowering of T_1 and T_2 by a peptizer is greater the lower its melting point. Oleic acid is much more active than stearic, and cresol more than phenol.

The case of commercial lime-soap greases is interesting and complex. Pure calcium stearate segregates from oil suddenly at 119° C. This would appear to be its T_2, but it is difficult to establish this, owing to the fact the calcium soaps form very soft, sticky crystals, which make differentiation of plastic and crystalline phases difficult. The practice of adding water to prevent this segregation and to homogenize the soap–oil

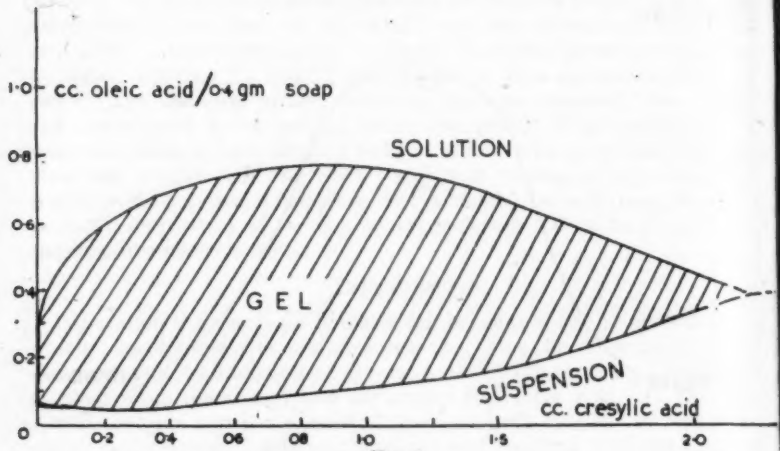

FIG. 4.

SODIUM STEARATE IN NUJOL AT 17° C.

system is certainly a case of peptization. How far the action of the water consists of hydrolysis, so that the active peptizer is fatty acid, is not clear; but some hydrolysis does take place and can be set back by the presence of free $Ca(OH)_2$. This need for peptizing calcium soaps is responsible for the low melting point of lime-soap greases compared with the very high melting point of the soap alone.* I do not think that this problem of making high-melting-point calcium soap greases is insuperable if suitable calcium soaps and suitable peptizers were used.

EFFECT OF MIXING KATIONS.

Suggestions have been made for making greases with more than one metal—*e.g.*, mixing calcium with soda soaps, lithium with other metals, and barium with calcium. The writer has carried out a few experiments

* Decomposes above 300° C. without melting.

on this point, and has found powerful mutual interaction between kations, accompanied by marked loss of consistency. It is possible that this could be offset by increasing the percentage of soap if the consistency of the mixed product were to show specially desirable features. However, the evidence available suggests that mixing metals is a thoroughly bad procedure. Calcium stearate loses body badly with lead stearate, and almost as badly with commercial aluminium stearate and silver stearate. Cobalt stearate also cuts out gelation and shows marked colour change peculiarities. Cobalt soaps, alone, form at temperatures, above 140° C., extremely deep blue solutions in Nujol. In the presence of excess of calcium stearate only a very pale blue colour develops in heating. The minimum consistency of mixtures occurs at the equimolecular ratio and the T_1 curve for mixtures is of eutectoid form.

The Physical State of the Soap Below T_2.

I have already mentioned the differences between the micro-crystals of soaps deposited from dilute solution and the paste formed at higher concentrations. There would appear to be no difference in phase but there are certainly differences in size of crystallites, and possibly habit. Some gels, in cooling, merely become opaque at T_2 with little loss of body, whereas others show a big difference. Lithium stearate shows very little, the palmitate not much, but the myristate shows syneresis with about 30 per cent. of the oil clear after a few months, and the laurate has become a suspension of micro-crystals. One would expect little change of consistency of greases below their T_2, since the contribution made by the soap is of a temperature-independent nature, but there is this unknown factor which determines whether a paste below T_2 remains homogeneous or whether it undergoes syneresis and bleeding or not. The condition for minimum syneresis is obviously that its contraction should be minimal. Whether this contraction is thermal, or whether it is a residual effect due to incomplete contraction at T_2, where the large thermal contraction occurs,* remains to be found. It is again quite clear that the behaviour of single pure soaps must be determined before the behaviour of mixtures can be understood. It is particularly unfortunate that the soda and calcium soaps most used in greases are both highly susceptible to small amounts of water. The equivalent of water required for complete hydrolysis of a soap is of the order of only 6 per cent. There is no simple and accurate method for determination of water in soaps, especially where it is strongly bound to the soap. The soaps which can be prepared in a high state of purity most easily are those which form complexes with pyridine—*e.g.*, cobalt and copper. The pyridine complex crystallizes from pyridine in hard, well-defined crystals from which the pure soap is recovered by heating *in vacuo*. Aluminium tri-stearate is also easily prepared in a state of high purity. With most soaps, the chief impurity to be avoided, both on grounds of difficulty of removal and on account of its peptizing effect, is fatty acid.

The origin of the gelation of soap in oil and the other phenomena described here is not clear. To explain the high viscosity I have suggested

* *Loc. cit.*, p. 4.

that the gel has a micellar structure such as is shown in Fig. 5. Association is by –COOM groups, which are separated mainly by thermal dissociation at T_1. Such a fibrillar micelle would explain elasticity such as the aluminium soaps show, but there must be some special factor also operating which differentiates these from other soaps. It is of interest to note that the three aluminium soaps, tri-, monohydroxy-di-, and dihydroxy-mono-, of any fatty acid are very similar in their behaviour and in their T_1 and T_2 values. Co-ordination is an obvious possible cause. It has often been suggested that co-ordination is responsible for the association of fatty acids in pairs and for the fact that the oxygen in the $-C<^{O}_{OH}$ group shown as ketonic does not in fact behave as ketonic either in the acids or in their esters. In this light, it is of interest to note that the colour of soaps, such as those of copper, cobalt, nickel, uranyl, etc., is that of the

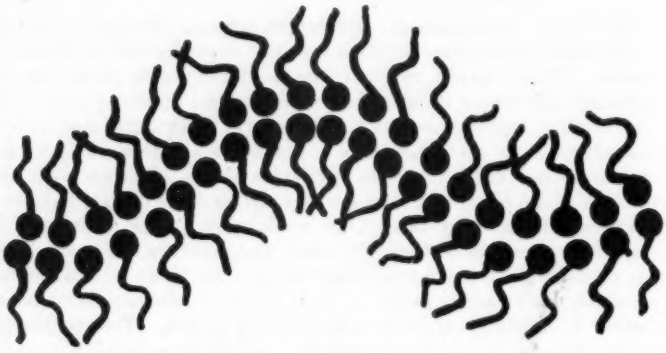

FIG. 5.

ion. However, the suggestion of co-ordination is no more than a tentative idea which might be tested, but I doubt whether it is of practical importance to the grease-maker just yet.

RHEOLOGY OF GREASES.

I have not said much about the rheology of greases, but it will be clear, I think, to this meeting that the considerations which I have outlined have a fundamental bearing on the interpretation of measurements of viscosity, plasticity, and consistency of greases. I suppose that there is no use of greases which does not depend on their special rheological properties. Even where the grease is used as a "sponge" feeding oil, it is clear that the thinnest oil suitable for the lubrication should be used and the consistency of the grease raised by the soap part of it. The fact, already mentioned, that the gel phase can be dispersed in oil by mechanical means without heating above T_1 is made use of in the preparation of all greases. The almost complete lack of published data on the temperature–flow relations of greases is most surprising, until one remembers that most grease lubrication is at low temperatures, and that the thermal stability of common greases is somewhat poor. I have pointed out that the gel

phase has the highest viscosity, but this does not mean that this phase is the best for most purposes. In fact, some solid soap is required where rigidity is useful—*e.g.*, in dirt excluding lubrication. There is no doubt that soaps do impart useful lubrication qualities to oils at higher temperatures, but this field is largely unknown ground. Measurements of the variation of viscosity with temperature are not only interesting practically, but should be of theoretical interest in determining the energy of activation of the flow of the different phases. In Klemgard's book are two sets of results which I have plotted. Fig. 6 is for a worked soda-soap grease at approximately constant flow rate. Whether the peak corresponds

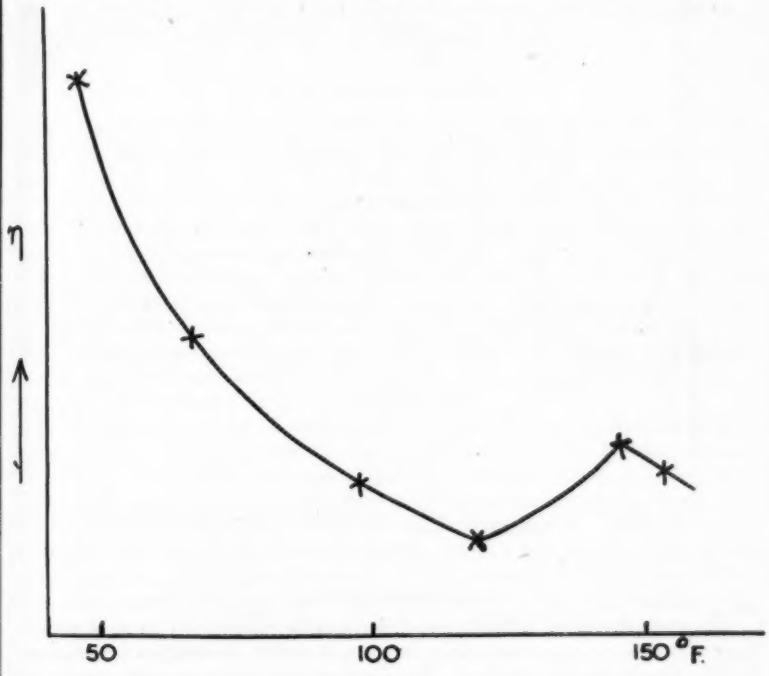

FIG. 6.

with my T_2 it is impossible to say, but the curve is such that one cannot doubt the complexity of the changes. Fig. 7 is for a soda-base Chrysler gear-grease. Curve 1 gives the results, and curve 2 gives these plotted as $\log \eta$ against 1/T Abs. Here again the results are incomplete, but the change in energy of activation of flow is startling. It would be of greatest interest to see results for a pure soap. It is possible, however, that the results below T_2 would be best interpreted on hydrodynamic grounds along the lines worked out by Robinson and the writer for long, thread-shaped particles.[8] If the soap crystallites are anisometric, they will be thin plates in most cases, although needle-shaped crystals are seen quite often in lime-soap greases.

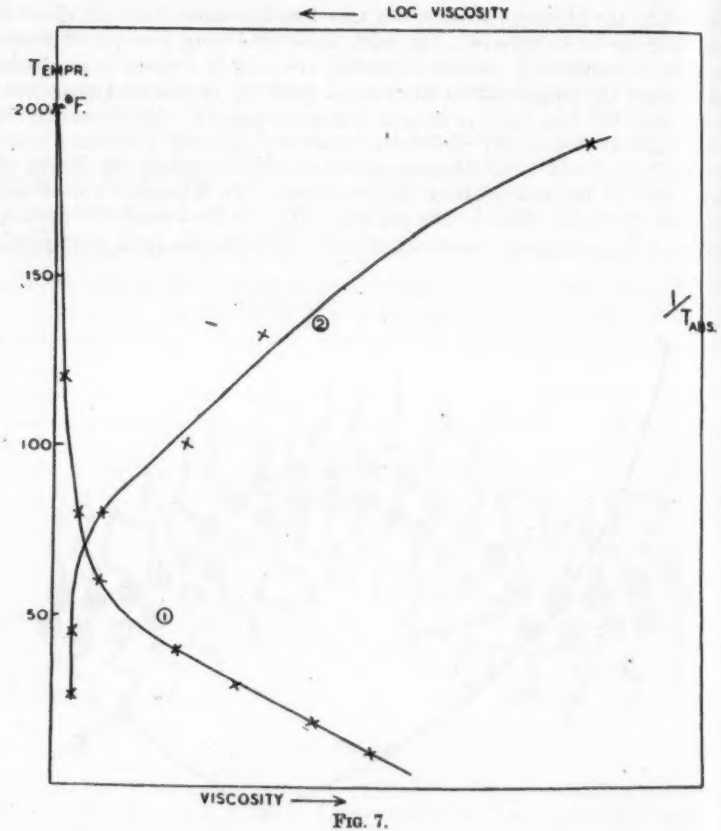

FIG. 7.

Acknowledgment.

The work described in this paper was mainly carried out in the Laboratory of Colloid Science, Cambridge, as part of certain researches undertaken for the Fuel Research Station. The observations on the mixing of kations and on the Lithium soaps formed part of certain work done for the Ministry of Supply Advisory Service on Lubrication. Figs. 2 and 5 are reproduced here by kind permission of the Faraday Society.

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INSTITUTE OF PETROLEUM AND BRITISH RHEOLOGISTS CLUB.

A JOINT meeting of the Institute of Petroleum and the British Rheologists Club was held at Manson House, Portland Place, W.1. on Wednesday, 18th April, 1945. At the afternoon session the chair was taken by PROFESSOR E. N. DE C. ANDRADE, F.R.S. (President of the British Rheologists Club) and the evening session was presided over by PROFESSOR F. H. GARNER, O.B.E. (President of the Institute of Petroleum).

AFTERNOON SESSION.

The CHAIRMAN (Professor Andrade) said that rheology was the branch of science that dealt with physical and structural aspects of flow in substances of all kinds. This was wider than the study of viscosity. A viscous liquid was a substance which would yield under a stress, however small, if left for a sufficiently long time. There were substances which were quite capable of sustaining a small stress for a practically infinite time, but if that stress was increased beyond a certain value, flow occurred. It was usual to call these substances plastic. The science of rheology dealt with plastic as well as viscous substances. Whereas in ordinary liquids the flow went on permanently at a fixed rate under a given stress, other substances such as metals hardened with time when flowing under stress. These also, however, were included in the study of rheology.

In the case of certain viscous liquids the rate of flow, or, more strictly speaking, the velocity gradient, was proportional to the shearing stress. These were the so-called Newtonian liquids. With liquids of another class the velocity gradient did not vary linearly with the shearing stress, but was a more complicated function, which had to be determined. In both these cases the rate of flow, however, did not depend on the previous history of the substance. There were, however, other liquids which, if left alone after flow had ceased, changed their properties with time. The thixotropic solutions, in which the structure, and hence the flow properties, was particularly susceptible to mechanical treatment, were an example of this behaviour. Particularly complicated was the flow of solids, especially metals, in which under constant stress the rate of flow decreased with time in a regular manner. All these classes of flow were the subject of rheology.

Even among liquids, then, there were various complications, and he would describe oils as among the difficult liquids. He took as a test of a simple liquid the temperature equation

$$\eta v^{\frac{1}{3}} = Ae^{b/Tv}$$

or its simpler form

$$\eta = Ae^{b/T}$$

If a liquid obeyed this law it meant that its molecular state of aggregation did not change with temperature. Thus the viscosity of pentane, hexane, and the other simple paraffins was closely represented by it, but that of

water was not, the reason being that at lower temperatures the simple H_2O molecules were associated into larger molecules, the degree of association diminishing as the temperature rose. The viscosity of ordinary oils did not, he believed, in general obey this relation, possibly because they were mixtures of pure chemical substances.

He hoped that he might be forgiven if he issued a warning against trying to draw conclusions from the agreement or failure of any theoretical formula to represent the variation of viscosity of a liquid, without close examination of the conditions contemplated in the theory. The fact, for instance, that any given theoretical formula deduced for the simplest type of liquid did not fit water was in favour of such formula, not against it.

THE PRECISION AND ACCURACY OF VISCOMETRY USING B.S.I. TUBES.

By the Viscosity Panel of Standardization Sub-Committee No. 6—Lubricants (see pp. 239–247).

DR. G. BARR, in presenting this paper on behalf of the Sub-Committee, said that although he was doing so as its Chairman, practically all the analysis of the data obtained had been done by Professor Garner and Dr. Nissan.

The CHAIRMAN asked whether dissolved air in oils might affect their viscosities.

MR. H. RUFFELL said that the time of flow of an oil in a viscometer as determined in Britain, when compared with the time of flow of the same oil in the States, must differ with the acceleration due to gravity. This is not constant, but varies over the earth's surface, the variation being of the order of 979–982 cm./sec.^{2} It seemed to him that, this being a direct factor, it must to some degree affect the times of flow.

DR. RANKINE said that it might be that 0·1 per cent. was a possibility, but it would be dangerous if carried to extremes. If New York was about 40° latitude and London 51°, it might suggest material for a useful prediction.

The CHAIRMAN said that apparently it might be a question of 0·1 or 0·2 per cent.

MR. C. I. KELLY said that when he was last in the laboratory, about ten years ago—the oils used for standard viscosity determinations were given a certain pre-heat treatment to reduce the possible effects of hysteresis. Had that been taken into account in all the collaborating laboratories? Or, had some warmed the oils before using them to fix their thermal history and had not reported to the Institute's observer?

Again, there was the question whether the thermostat's medium had in different places been agitated more vigorously than in others. It might be that excessive agitation produced severe vibrations which, transmitted from the agitator through the thermostat's frame to the rigidly held viscometer, might vitiate the results.

Thirdly, could a certain amount of the differences between laboratories be ascribed to response-differences between timepieces? This was over and above the varying time-lags due to the differences between the reflex-action of individuals and to the inability of all observers to make up their minds

with the same alacrity in a fixed set of circumstances. In some laboratories electric-impulse clocks were used which could subdivide the second with great accuracy. How would this type in one laboratory and the uncertain stop-watch in another affect agreement between laboratories using the same oils and viscometers?

Finally, he would ask, in the endeavour to keep this matter rooted in realities, was it necessary to strain to such an extent after fine limits when the user of oil did not care whether its viscosity varied 1 per cent. either way about a mean figure?

Mr. D. L. Samuel said that in regard to the query raised by the last speaker, he would point out that viscosity indices were now included in many specifications, and very often a minimum V.I. was specified. If viscosities were not determined accurately there would be a considerable spread in the V.I. values obtained therefrom. Producers would therefore have to refine to a higher V.I. than was necessary to be sure of melting the minimum specified, and this would increase their costs.

Dr. A. H. Nissan suggested that they should not always make the basis of their consideration the fact that somebody must use the oil. Accuracy had its own justification for existence on theoretical grounds, and he thought that the paper served its purpose, not in finding a use for the accurate viscometry, but in discussing the accuracy of viscometry obtaining at the present time.

The Chairman pointed out that in engineering work there was always striving after greater accuracy than was actually needed, instancing the measurement of length. He thought it was well that it should be so.

Mr. J. C. Cragg said that he had been interested to hear Dr. Barr comment on the low flow times of Oil 40 in the No. 2 B.S.I. Tubes from which the ratios shown in Table I were calculated. The actual flow time of Oil 40 in Tube No. 156/9 would be approximately 80·6 seconds, in Tube No. 150/9, 113·1 seconds. If the object in view was to determine the accuracy of viscosity measurement, he thought that the generally accepted correction, $\frac{c}{t}$, should be applied to the flow times; this would amount to approximately 0·03 in the case of Tube No. 156/9 and approximately 0·02 in the case of Tube No. 150/9, which for a viscosity of approximately 5·15 cs. would amount to a difference in viscosity of 0·2 per cent.

The dynamic test described, he thought, was not conclusive, as the oils selected to carry out this test were not of the same order of viscosity as those tested by the various co-operating laboratories. It had previously been shown in a recent paper by one of his more learned colleagues and himself that the calibration constant of a B.S.I. viscometer might vary within the range of the instrument. Dr. Steiner had shown by comparing the flow time of various oils in two No. 3 B.S.I. viscometers that the difference in flow time is not always consistent. With a flow time of 54 seconds a time difference of 4·47 per cent. was encountered; at 278 seconds the difference was 5·06 per cent. and at 642 seconds, 4·87 per cent. As one of these viscometers had previously been proved to have a reliable constant, this meant that the other instrument must be unreliable. In other words if it were calibrated for a flow time of about 278 seconds it would be unreliable for determining viscosity both above and below that figure.

On the general subject of viscometry he thought it might well be stated that if the industry now had to use viscometers capable of more accurate measurement than the Redwood, consideration should be given to the suspended level type of instrument. In his opinion it was far more satisfactory than the B.S.I. type for routine measurements of V.I.; for one thing the question of an exact amount of oil did not arise.

Dr. G. W. Scott-Blair said that someone had suggested that reaction times enter into this. He did not think that was very likely. Supposing the observer was one-fifth of a second late in noting both the start and the end of it, surely any variations in time of fall due to reaction time would be very small and randomized among the observers. One could hardly suppose that the reaction time of the Americans was much longer than our own.

Dr. L. A. Steiner said that reference had been made to the work he had carried out, and perhaps he might be permitted to make a few remarks, particularly to explain the conditions under which his tests were carried out.

There could have been no possible error in temperature; any error which there might have been in the absolute value of the temperature—*i.e.*, about $\pm 0{\cdot}01°$ C.—must have been eliminated with a very fair degree of completeness, as the measurement was only a relative one. Time measurement had been conducted in a very similar manner; an electronic instrument supplied the same impulses, at a rate constant to $\pm 0{\cdot}02$ per cent., to a number of time recorders, of which six were operated by the same observer. This seemed to eliminate any error in the relative accuracy of the time measurement. When viscometers were compared by different stop-watches there was an appreciable error, due to the difference in the rate of the stop-watches. The level had been roughly adjusted in the evening; in the morning it had been checked and adjusted accurately, so that there had been no error due to wrong adjustment of level.

Nevertheless, two viscometers, compared under exactly identical conditions, had shown that the ratio of efflux times—when plotted against viscosity—was a curve, and not a straight line as expected, which meant exactly that it might well be that at two points a number of viscometers were identical, but not necessarily so in between or outside that range.

Perhaps he might add something else—namely, that the fact in itself that selected viscometers were exactly identical did not necessarily mean that they were correct. It might be just as safe to assume that they were wrong. When he compared two viscometers and found that they were—by chance—identical in the whole range, with a margin of error of $\pm 0{\cdot}02$ per cent., he was very careful to point out that that did not mean that both those viscometers were correct; it merely meant that both were equally wrong.

The Chairman: What do you mean by viscometers being "correct"?

Dr. Steiner replied that a viscometer would be regarded as correct if its calibration constant was independent of the efflux time. In the official formula the calibration constant is given as the ratio of viscosity and the efflux time plus kinetic energy correction, and is assumed to be a constant. While this is true roughly, it is not true exactly. There are small differences for which he had at the present moment no sufficient explanation, but that did not make any difference to his declaration that these discrepancies did exist, and he was not the only one who put forward that opinion.

If there is experimental evidence for assuming that viscometers of the same size in general did not behave as they were expected to behave on mere theretical considerations, in his opinion there is no reason to assume that viscometers of different size would do so. The dynamic quality test relies on the fact that a number of viscometers of the same size and design have identical ratios, while the real problem is whether viscometers of different size and design have correct ratios or not.

Mr. E. J. Dunstan said that as they were dealing with very small limits it might be pointed out that in the case of Oil 25 in Table III the Standard Inspection Laboratory obtained a lower result than the National Bureau of Standards, and in the case of Oil 39 a higher result. Again, it might be pointed out that in the case of Oil 38 the N.P.L. obtained a higher result than the Texas Oil Co., although attached to the N.P.L. finding there were the figures 1–5, as to the meaning of which he was not clear. He suggested that some other errors might be looked for than gravitational forces.

Mr. C. E. Kendall said that it seemed to be assumed in all this type of work that the materials used were Newtonian liquids. It was not inconceivable that a concentrated sucrose solution may show a very slight degree of structural viscosity, and since the wall stress was approximately doubled in stepping up from one instrument to the next in the series, there would be a cumulative error in stepping up two or three times. With regard to oils, there was the possibility not only of structural viscosity but of thixotropy to be considered. R. N. Weltmann (*Industr. Engng Chem.*, 1943, 15, 424) claimed that many oils were thixotropic when examined in a rotating cylinder instrument; although thixotropy could not be studied in a capillary instrument, the possibility of the error caused by this phenomenon should be borne in mind.

Dr. E. W. T. Mardles said that he wished to be associated with the remarks of Prof. Andrade and others when they said that a lubricating oil was not the best kind of calibrating liquid. Hydrocarbons of higher molecular weight tended to form temporary aggregates or clusters of molecules (cyboma) and these could flocculate into a weak three-dimensional structure on standing, giving the oil a very slight but measurable rigidity. The small variations in viscosity results by different observers might well be due to variations in rigidity of the calibrating oil due to thermal history, shaking, etc.

Dr. A. Lahiri said that it had been found that many oils did show slight rigidity, and that rigidity varied with the history of the oil. In thicker oil it showed up markedly, but in thinner oil it was not so readily demonstrable.

Dr. Barr, in replying to the discussion, said that the Chairman had referred to the effect of dissolved air and moisture in the oil. It was rather a commonplace in viscometry that if the viscometer were filled up all ready for a run and left until the next morning, a different answer would be forthcoming from the one which would have been obtained right away. Another point in that connection was that in a certain No. 3 Tube, 60 per cent. sugar had been used, and at intervals that tube was used to measure the viscosity of an oil for calibrating other tubes. In many cases unusual readings were found, and after they had changed over it required repeated cleaning before they could get back to their former value. He could not imagine any possible film of insoluble material being large enough or thick

enough to alter the mechanical conditions of the tube, but it might affect the interchange of air and water.

On the point of thermal conditions, he stated that in their viscosity determinations they had not carried out the procedure for eliminating hysteresis by heating the oil prior to the determination.

DR. A. H. NISSAN, in a written contribution, said that in discussing the accuracy of viscometry it was suggested that the 0·36 per cent. consistent deviation observed between the results of American and British viscometry systems might be due to the difference in the value of g in the States and Britain.

Detailed considerations show the variation in the value of g cannot be the cause of the observed deviation. In relative viscometry we measure the time, t, for a standard quantity, Q, to flow through tubes of standard length, L, and diameter, D, under a standard head, H, at constant temperature. Assuming for the moment kinetic energy correction is negligible—i.e., for times of flow exceeding 100 seconds—and that the Couette correction is a certain number of diameters to be added to L to render it an effective length L', we get for an oil

$$t_1 = K\frac{QL'\mu 1}{H\rho g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K = constant
ρ = density
μ = viscosity

or $$\frac{\mu_1}{\rho_1} = K^1 g t_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

However, we determine K^1 by calibrating the instrument, *in the same laboratory*, by a fluid the viscosity and density of which are known or assumed. Thus,

$$\frac{\mu_2}{\rho_2} = K^1 g t_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or $$K^1 g = K^{11} = \frac{\mu_2}{\rho_2 t_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus, in equation (2) we insert $K^{11} = K^1 g$ to evaluate $\frac{\mu_1}{\rho_1}$, *i.e.*

$$\frac{\mu_1}{\rho_1} = K^{11} t_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence, $\frac{\mu_1}{\rho_1}$ will be independent of the variation of the value of g.

Taking kinetic energy effects into account results in exactly the same conclusion.

THE TESTING OF GREASES FOR BALL-BEARINGS.

By S. R. PETHRICK, B.Sc. (see pp. 248–254).

This paper was presented by the author.

MR. BELL said that the paper was most welcome at a time when increasing attention was being given to the question of developing and standardizing

laboratory test methods for evaluating the service performance of greases. The author had perhaps tended to over-simplify the problem of evaluating greases when he suggested that such test methods should be classified under two main headings—namely, test methods applicable to greases for use at low speeds and moderate temperatures, and test methods applicable to greases for high speeds and high temperatures. Would this actually cover all service requirements? He would suggest that the problem involved the question of both low- and high-speed conditions at both moderate and high temperatures.

Both in his general classification of these test methods and his consideration of apparent viscosity, the author indicated that normal lime-base greases were only suitable for use under low-speed conditions. Admittedly at high rates of shear the apparent viscosity of a lime-base grease approximates to that of its mineral oil component; but this was also true of many soda-base greases which as a class were indicated as suitable for high speed conditions. The apparent viscosity of the grease remained low only for as long as it was subjected to the high rate of shear. But the effect was not permanent, and the grease would normally more or less revert to its original state when the shear force ceased to be exerted. There were greases which might undergo permanent changes in consistency when agitated or worked in a bearing, due to breakdown of the grease structure, but this should not be confused with normal flow characteristics at various rates of shear.

Apart from these considerations, service tests showed that normal lime-base greases could in fact be used for high-speed applications at moderate temperatures. For example, a typical lime-base grease has been used for a considerable time with complete satisfaction for the lubrication of ball-bearings running at 25,000 r.p.m. The author had stated that cohesion and adhesion of most lime greases were very similar. Was this generalization quite true? Would not the viscosity of the mineral-oil base influence these particular characteristics, as it would, of course, the apparent viscosity at both low and high rates of shear?

Of the various types of stability met with in service, whilst resistance to oxidation and the tendency of the grease to separate oil are most important, the question of agitation or working permanently breaking down the grease structure is also of considerable importance. He felt that the question of measuring the tendency of a grease to separate oil under various service conditions is very involved, and doubted if stability tests based on capillary action would provide a complete answer. Stability tests depending on capillary action and carried out at relatively low temperatures were no doubt indicative of the tendency to separate oil when a grease is packed into a bearing and the bearing stored in a cardboard container. An accelerated test carried out at unduly high temperatures might confuse the issue by bringing in other factors, such as the question of heat stability.

Apart from this particular aspect of storage stability, we were concerned with three other forms of stability involving the separation of oil—namely, normal storage stability, pressure stability, and heat stability. Oil separation in normal storage conditions appeared to be caused by a small pressure gradient in the grease due to its weight. He suggested that oil separation in general was more likely to be due to a slight pressure gradient effect than to capillary action.

MR. C. E. MOLD said that the majority of tests, drop-point and the like, would be ultimately classified with the similar forms of oil test which were used years ago, but were now falling out of favour. The introduction of a " court of appeal " was, he was sure, the correct line. Mr. Bell had raised the question of classification into low-speed and moderate temperatures and high-speed and high temperatures. The use of ball-bearing greases in the main would be for moderate temperature and fairly high speed. He imagined the consumption for industrial, generating plant and large bearing work of that kind where temperatures were moderate was probably the most important factor, certainly in peace-time, and there was a danger that by looking at Service requirements, normal requirements would be overlooked. For that class of work stability was not the main factor, and the emphasis upon a standard of torque for a period of running was much less important, and in fact probably detrimental. For conditions where temperatures had no business to rise to a dangerous height one did not want to preserve this high torque. He had had many cases of lengthy test runs in which the torque on the bearing had been in fairly close agreement with the torque on the oil-lubricated bearing.

In the design of the plant for the author's test it was possible that the bearing set up was such that some of the torque was attributable to the side bearings of the drive, and he wondered whether the author had in mind any modification so that there could be no twist. Another but minor question was whether the heat regulation of the device was satisfactory. It did not seem, as shown in the photograph, that there was any definite form of control. He felt that this type of apparatus was characteristic of what would be necessary for testing apparatus.

MR. WEBBER said that Arveson (*Industr. Engng Chem.*, 1932) observed that lime grease could be forced through the capillary of the viscometer, the lowest point of charge being slightly above that of oil content. The apparatus now described could be used for different speeds and at different temperatures, and he thought the reason why the temperatures and speeds mentioned had been selected was because of the difficulty of securing satisfactory greases. The first machine of this type was designed and built in 1938, and was completely described in papers in September 1941, in the *Transactions* of the National Lubricating Institute.

The author had commented on the fact that one grease, which behaved well in the torque tests, when heated in the presence of a copper strip showed a marked degree of liquefaction. It would be interesting to know whether the liquefaction was not shown up in the bleeding test.

MR. E. A. EVANS felt that the author had served a very useful purpose in bringing forward this apparatus, even if only as a research apparatus. It would have the great advantage of making the grease-makers think a little more seriously about the properties of greases which had not been studied, and if the apparatus was going to improve the quality of greases, the price would automatically adjust itself by the law of economics.

The CHAIRMAN said that as he understood this apparatus, its purpose was to find out what greases were satisfactory, and then to find out what were their physical properties, and so later on to establish what physical properties were desirable in a grease.

MR. D. L. SAMUEL said that this was a valuable contribution to the subject

of grease-testing. He agreed that new tests were required, since existing methods gave little information as to the quality of greases.

Accelerated tests were often necessary, and were used to a great extent in examining petroleum products. However, with a material like grease one had to be particularly careful how far one accelerated.

It was generally agreed that greases should not be used at temperatures in the neighbourhood of their drop point. A test such as described by the author, in which a bearing packed with grease is heated to 10° C. below the drop point for a week, is therefore of little value, and is far removed from practice.

Dr. Scott Blair mentioned that there had been sent to some members of the Rheologists Club, through the courtesy of the Soviet Embassy, the *Proceedings* of a conference held at Moscow in 1941 on the viscosity of liquids and colloidal solutions. Some of the authors of the papers were rheologists well known to British workers on the subject. Among the writings were several papers on greases, also a number on the flow-anomalies of oils; and on the viscosity index, which came in for a great deal of criticism. If he were himself a grease rheologist and did not know any Russian, he would feel that he would want these papers fully translated into English. They were really very valuable to any petroleum technologist.

Mr. Pethrick said that concerning the point raised about the classification of greases he was afraid the bearing manufacturers were at fault. Most bearing manufacturers worked for low speeds. With regard to stability, he had always felt that the stability of the grease in the bearing was rather more important than the stability of the stock grease on the shelf. He had had a good deal of trouble to ensure that bearings which had been packed with grease had remained in good working order over a long period. With regard to Mr. Mold's point, he had desired to make it clear that the high torque merely applied to greases which were required for operational use.

Mr. H. W. Chetwin, in a written contribution, said it had become increasingly obvious of late that the conventional methods of testing, or, more accurately speaking, examining grease, are quite inadequate to permit of its proper evaluation as a lubricant. He shared the author's unflattering opinion of the drop-point and penetration tests, to which he would add the stability or separation test. Apart from the over-riding consideration that those tests are of little value taken separately, because they are really interdependent, the results obtained therefrom are not absolute, but are relative to the instrument by means of which they are taken. The melting point of a grease may be said to vary several degrees C. when taken by different methods; the penetration test fails to throw any light on the important factors of adhesion and cohesion, and the stability (heat test) which has become a playground for experimentalists is, he suggested, the most arbitrary of them all.

The inadequacy of these tests is well illustrated by the recent experience of the trade in respect of certain specifications for grease of the highest importance. It is no secret that in some cases grease which had been accepted, and properly accepted in prevailing conditions of testing, as conforming to the specification, had proved unsatisfactory in use. Therefore he welcomed an instrument which reproduced, at least in great part,

working conditions, and in one operation provided data which included the effects of heat, friction, and centrifugal action.

On the other hand, regarding it from the point of view of the grease manufacturer, he was not so happy about it. In the first place, one had to be convinced that results obtained by this instrument could be correlated with those derived from other similar apparatus: were we going to be in the position, if this method of testing is adopted, of having to provide a whole collection of competing instruments to meet the preferences of various grease users, or was someone going to prepare tables of equivalents? Then he foresaw a vast increase in the time required, not only for the carrying out of the tests, but for extensive research involving investigation of the effects of using many different combinations of materials and methods of manufacture to obtain results which, after all was said and done, must be in many instances academic, inasmuch as in present conditions perfectly satisfactory lubrication was being obtained, in the great majority of cases, by grease which might very well be condemned as a result of tests applied by such an instrument.

He felt also that the instrument may be limited in its scope. It is a matter of experiment to determine, for example, how far the type of housing of a bearing affects the results. But the principal reason for his apprehension was that the evaluation of grease by this, or other similar instrument, would lead to greater specialization. The author says that "after remounting the bearing, the temperature is to be raised to a value slightly higher than that to which the grease is to be subjected in service," but he should realize how rarely the manufacturer possesses or is able to obtain such details of use, and he envisaged the demand for greases often in small quantities made to comply with a test taken in one of the many combinations of circumstance to which the instrument lends itself.

Finally, he could not overlook the warning conveyed by the author that "For most greases the above tests should reveal any tendency towards instability," and he mentions an exception—there may of course be others. It is a cautious statement and one which Mr. Chetwin thought might well be kept in mind when considering tests taken by the method described.

MR. PETHRICK, in reply to Mr. Chetwin, said he would be delighted if the introduction of the torque apparatus lead to extensive research, since he could not share his complacency with regard to the performance of large numbers of greases in precision mechanisms. Recently there had been far too many instances where, owing to the deficiencies of greases, cumbersome oil circulation systems have had to be installed in otherwise compact mechanisms.

As for Mr. Chetwin's apprehensions regarding specialization, he felt that owing to the non-practical nature of present-day tests, specialization in the form of selection of one particular product was already a general practice. This led to great difficulties when large quantities of grease were required. If a torque test in some form or other was adopted, a greater uniformity in quality could be obtained, and users would accept supplies from a larger number of sources.

With regard to the question of instability, the exception mentioned in the paper may reflect on the 100° C. heat test rather than on the torque tests.

EVENING SESSION.

The CHAIRMAN (Prof. F. H. Garner, O.B.E.) said that the wide range of subjects covered in these two meetings illustrated the breadth of subject-matter covered by rheology. When the meeting was first suggested by the Institute in the middle of last year, it was rather hoped that there might be included some papers on war developments of special interest to the British Rheologists Club, but in this expectation they had proved to be somewhat too optimistic or too premature. The first paper was being presented by Dr. Nissan, as Mr. Hardiman was abroad; it was perhaps appropriate that the first paper of the evening session on Rheology should be presented by a member of the Institute from Birmingham. For Dugdale in his *Antiquities of Warwickshire* (1656, p. 653) tells us that Edgbaston is "on the Brook called Rhea . . . which signifieth to run or flow, and seemeth to have its originell from the Greek word ρεω."

A RATIONAL BASIS FOR THE VISCOSITY INDEX SYSTEM. PART I.

By E. W. HARDIMAN, B.Sc., M.Inst.Pet., and ALFRED H. NISSAN, D.Sc., M.Inst.Pet (see pp. 255–270).

Mr. J. W. HYDE agreed that the discussion could not centre round the value of the relative merits of the Viscosity Index, since it has been pointed out by the authors that the Dean and Davis system has been widely accepted. Complete agreement must, however, be obtained on the formula used by all workers in order to ensure uniformity. It therefore follows that before the authors' modifications can be used they must be accepted by the standardization bodies of the A.S.T.M. and the Institute of Petroleum.

It has long been realized that the Dean and Davis V.I. system for measurement of viscosity slope was far from sound. The more important of the reasons for this are :—

1. Increase in temperature viscosity slope is not directly proportional to V.I.
2. At V.I. below *O*, which are not discussed by the present authors, small changes in slope are represented by large changes in V.I.
3. The V.I. is not an additive function.

This latter is an important point to the research and commercial worker, and for this reason Walther claimed that the viscosity pole was an additive function. Any future work on factors to measure viscosity temperature slope should be directed to the provision of an additive function capable of being converted to V.I. by a set of suitable tables, and that the value of this function should, if possible, bear a substantially direct relationship to the decrease in viscosity temperature slopes.

DR. NISSAN agreed that if something could be found which was a direct function of the temperature coefficient of viscosity under all circumstances, and something that was additive, a better system would be forthcoming than they had at present. There was some doubt that these would be achieved in the near future, and consequently he thought that even an arbitrary value would probably serve the purpose better for the time being. He thought they must rely upon their scientists to give the mixture law for viscosities, which was not as yet fully understood even for pure liquids.

MR. C. PAYSANT said that if they tried to picture what was happening in the oil or solution tested, the " quality " of the oil might not mean the same thing to Dr. Nissan as to others. In the oil industry, quality (in the present context) might be looked on as the chemical nature or kind of molecule making up the major part of the oil; " paraffinic " or " aromatic " nature might be the main virtue represented by V.I.

This quality of the major portion of the oil would be one factor determining V.I. In addition, the presence by accident or design of large molecules or bodies in the oil would alter the V.I., as a rule improving it. Again, there might be a semblance of rigidity caused perhaps by free energy in some constituents.

These three factors, and possibly others, all contributed to the overall viscosity–temperature relationships. He wondered whether, by mathematical " tricks," some of these variables were, in effect, cut out when obtaining the simplified formula; the new index would then refer to " quality " (chemical nature) of the major part of the oil, but the effect of rigidity, presence of large particles, etc., would be eliminated. If that was the case, then the new index, while very valuable as affording much information concerning the general chemical nature of the oil, would not tell the complete story to the manufacturer and user.

DR. NISSAN replied that the method of the V.I. was merely to take two values of viscosity and assume that these values were significant. It gave a constant, which they measured even though such a constant did not tell the full story. They might still decide that it was better to have that quality tested according to the assumption that these two figures were significant. There were other appropriate methods of measuring particular properties of oils in which one was interested. Oil was a complex substance. There must be so many tests, depending on the number of variables. The matter turned upon the acceptance of the first assumption that the viscosity change between certain temperatures was significant and that it was a measure of some quality of the oil. Then the modified V.I. would give a figure for that quality.

MR. E. A. EVANS hoped that every endeavour would be made to make this paper known in America. He felt that they would not be wasting time on a subject which in the next few years would become increasingly important. The same subject was raised in 1937 by E. Malscheart in the General Discussion on Lubrication (*Inst. Mech. Eng.*, 1937, **2**, 478), who suggested a modification of the established formula which would overcome this particular difficulty. Apparently that revised formula had been entirely forgotten. It was as follows:

$$100 \times \frac{w_0 - w_x}{w_0 - w_{100}}$$

where $w_0 = \log \log (\nu_0 + 0{\cdot}8)$

$w_x = \log \log (\nu_x + 0{\cdot}8)$

$w_{100} = \log \log (\nu_{100} + 0{\cdot}8)$

ν_0 = viscosity in cs. at 100° F. for zero viscosity index

ν_x = viscosity in cs. at 100° F. for oil under test

ν_{100} = viscosity in cs. at 100° F. for viscosity index of 100.

DR. NISSAN said that there were two objections to the modified formula

which Dr. Evans had given. It had always seemed to him that to take log after log tended to cover up variations which would appear in the natural function. The other objection was that the constant 0·8 apparently did not apply to its flow viscosity.

Mr. C. I. Kelly desired to ask a question which might not be directly related to the paper; it had to do with the way in which the V.I. was reported. The question was this: can the V.I. got by this new rational method be reported, so that the engineer designing a unit, or the user of the unit and oil, could calculate the oil's viscosities at any reasonable temperatures? The point of the question was that if the V.I. of an oil was given to engineers, they would say that they wanted to know how the oil would behave throughout the unit.

It seemed to him that the authors, with their new rational V.I. system, might be able to report the oil's V.I., together with a number denoting the oil's viscosity at an arbitrarily chosen temperature, so that the engineer could, with a simple viscosity temperature formula, calculate what he wanted. After all is done and said, the engineer was not primarily interested in an oil's V.I., as such; he wanted at least the oil's viscosities at temperatures often only known to him to be in the unit's working range of temperatures.

Dr. Nissen replied that certain work had been carried out in order to calculate the V.I. of an oil from the measurement of viscosity at any temperature range, and if that was successful it became a matter of manipulation of the curves to obtain the necessary graph. But, frankly, if he were working on the viscosity–temperature relationship he would try to arrive at the temperature relationship on fundamental rather than on empirical grounds, using the Index.

At present it is practicable to determine the viscosity of an oil at any temperature from the value of its viscosity at 100° F. and its V.I., by using the A.S.T.M. chart, since the two viscosities determining the V.I. give a straight line on this chart for all practical purposes.

Dr. W. E. J. Broom said that it was indeed interesting how a discussion on V.I. or some other method of expressing the change of viscosity with temperature, always seemed to provoke a very spirited discussion. He congratulated the authors on doing a good job of work in ironing out one of two difficulties which had already been noted by people who had to use the V.I. a good deal. He thought the authors' choice of the word "rational" an excellent one, and the way in which they had managed to make the rationalized system agree with the conventional V.I. system over the main part of the scale most in use, was a very great point in favour of their proposals. He had not had time to study the paper closely. He wondered whether the theoretically perfect oil gave the same answer whatever its viscosity, *i.e.*, would two theoretical oils of constant viscosity, *e.g.*, 10 cs., and 25 cs., have the same rational V.I.?

Mr. J. W. Hyde said that as is shown in Fig. 1 the Dean and Davis V.I. system is unsound at values greater than 130 V.I. This is, of course, not surprising, since it was originally designed to operate within the range 0–100 V.I. The authors have adjusted the Dean and Davis data to enable a more rational series of numbers to be obtained up to 180 V.I., as is demonstrated in Fig. 5. In this figure it is interesting to observe that the

line for 200 V.I. up to 25 cs. represents zero slope on the A.S.T.M. Chart, but that at values greater than this 200 V.I. means that the viscosity of the oil increases with temperature, or that the oil is better than "perfect" from the point of view of viscosity–temperature slope.

DR. NISSEN replied that the word "perfect" required definition. The change of viscosity with temperature was a function of the viscosity itself as well as the temperature, so that for two oils of the same quality one would expect that the higher-viscosity oil would change with temperature differently from the low-viscosity oil, because viscosity itself was a factor which came in. It was not merely a temperature change.

Thus, if

$$\log \eta = A + \frac{B}{T}$$

$$\frac{d \log \eta}{dT} = -\frac{B}{T^2} = \frac{A - \log \eta}{T}$$

showing that the viscosity temperature coefficient was affected by the absolute value of the viscosity ($\log \eta$) as well as the quality (A) of the oil. In other words, two oils of the same V.I. or quality, say, A, but of different viscosities at 100° F. would have different proportional drops in viscosities at 210° F. Hence if a 200 V.I. oil appears to be "perfect" when its viscosity at 100° F. is 25, more viscous oils of 200 V.I. appear to be slightly better than perfect.

COLONEL S. J. M. AULD, in a written contribution, said that both the President and Dr. Nissan particularly pointed out that the paper was not to be regarded as expressive of an opinion of the value of viscosity index nor as an indication of the relative usefulness of different systems of expressing viscosity–temperature relationship. He found this warning difficult to accept since it is not possible to improve the viscosity index system without strengthening its hold upon the petroleum industry. In this sense the paper must be taken on the basis of being an apologia for the system, and discussion may therefore logically be directed towards its relationship to other methods existing or capable of being developed. The paper is very interesting, and there seems little doubt the authors have ably done what they set out to do. This was apparently primarily to find an extension of the viscosity index system which would give numerical values on the same scale as at present, but outside the limits of 0 and 100 set by Dean and Davis on the basis of arbitrarily chosen reference materials. The incidental modification of the V.I. figures within the existing range is slight and may be immaterial.

The facts seem to be that the admittedly arbitrary range of 0 and 100 is retained as the basis, so that in this sense all other figures on the same scale but outside these limits continue to be meaningless. This is a pity in view of the apparent accuracy with which "η" may be expressed for oils of any fixed temperature range. The authors have therefore in their persuasive paper merely achieved at the best another set of figures like "angles of slope," "pole heights," or "ratios," stating what we know exists—viz., that there is a relationship between the viscosity of oil at one temperature and at another so long as the temperature–viscosity curves are smooth. It seemed to him, therefore, that the paper goes rather a long way round for

this purpose, and it is much more likely to achieve the effect of questionable value of perpetuation of the viscosity index system. This system is felt by many to be thoroughly poor. He would go further, and suggest that if it had been put forward, say, in Russian or German, it would not have been adopted either in this country or the U.S.A. Many of its limitations were known from the start, and another, to which the authors have made a slight reference in passing, is fundamentally objectionable. To wit, the fact that the Texan and Pennsylvanian oils chosen as references are themselves by no means constant in V.I. throughout the range of their component parts. He noted particularly during the presentation of the paper that Dr. Nissan agreed that viscosity index might be merely an elaborate method of presenting " η " on a larger scale. Surely this could be done by using a direct angular function, and it is noteworthy that the angle of slope is becoming progressively more popular in America. Once we had discovered the means of expressing viscosity–temperature relationships as straight lines he could not see why we should require a long list of nearly literally arbitrary constants for the expression of variation of slope of these straight lines. He personally would greatly welcome the direct interest of the president and of the present authors in a quest for an expression of suitable magnitude based on such procedure.

Mr. V. Biske, in a written contribution, said that whilst the data presented in this paper is of great value, and is of particular interest in the promise that it holds out of a method whereby the V.I. of an oil may be calculated from a knowledge of its viscosity at any two temperatures, which will fill a very long-felt want, it is nevertheless felt that even the system now proposed exhibits certain weaknesses when applied to oils having V.I. much in excess of 100.

Whilst the curves shown on Fig. 5 undoubtedly do away with the anomalous and absurd results of the Dean and Davis figures, when these latter are applied to oil of 150 V.I. and over, they nevertheless retain the " widening-out " of the numerical scale, whereby an increase of, say, 30 points in V.I. in the range of 150–180 represents a much more marked flattening of the viscosity–temperature curve than does one of from 50–80.

Although V.I. figures of 150 or over are, at the moment, of extremely limited applicability, any new system should look considerably to the future, when oils with very flat viscosity–temperature curves may be produced and, if possible, any numerical designation of viscosity–temperature characteristics should be such that a change in its value should always have approximately the same significance.

Furthermore, to deal with the case of the " perfect " oil, which does not change in viscosity with temperature, whilst this is at the moment largely a theoretical concept, the reported development of oils with reversed viscosity temperature coefficients may eventually make " perfect " oils possible. Whilst it is obvious that all such oils should have the same V.I., calculation on the basis of equations (10) and (11) yields values ranging from 195 in the case of an oil with a viscosity of 100 cs. to a limiting value of 218 for thinner oils.

There would thus appear to be still a good case for the use of the A.S.T.M. slope for oils of high V.I., expressing the latter either in terms of the angle of slope or else as a mathematical function of this angle.

Although it is not expressly stated in the paper, it is presumed that equations (10) and (11) are only intended for the calculation of viscosity-temperature characteristics for oils with a viscosity above a certain minimum value, since, if in equation (10) v_2 should ever equal unity (as can occur in the case of light products), then since $\log_{10}$ of one is zero, n becomes infinite, and equation (11) will therefore yield a V.I. value of the limiting figure of 218, irrespective of the actual viscosity–temperature slope.

Also, in certain cases where v_2 is less than 1, the V.I. calculated from these equations gives results which are not consistent with the viscosity–temperature relationship: thus for a liquid having a viscosity at 100° F. of 0·5 cs. and of 0·15 cs. at 210° F. a V.I. of 190 is obtained, whilst if the viscosity figures are 0·5 and 0·4 cs. respectively (*i.e.*, almost a "perfect" liquid), the V.I. figure given by the equations is 1–37, and in the case of a "perfect" oil of viscosity 0·5 cs. the figure is in the region of 700.

The AUTHORS, in reply to Mr. Biske, said that the numerical scale "widening out" shown in Fig. 5 was rather deceptive, since for the 150–180 V.I. lines, oils of high viscosities are shown, whilst for 0–100 V.I. lines only oils of lower viscosity values were possible on the plot. If comparisons were made at equal 210° F. viscosities, say 30 cs. at 210° F., it would be seen that the intervals for 10 V.I. units, whilst decreasing with increase in V.I., were not decreasing at a sharp rate. Of course there was no *a priori* reason why equal V.I. intervals should represent equal increments in the viscosity temperature slope on the A.S.T.M. or other charts, since there was, as yet, no explicit equation of performance of oils as a function of such slopes showing equal improvements in performance with equal increments in the slope. Indeed, oils of equal slopes on a temperature scale but of different viscosities were not of equal "quality," if by "quality" we mean that the oil belongs to a particular family of chemical compounds—the higher viscosity oils would have greater slope than the thinner oils even if both consisted of homologues of the same chemical family.

Hydrocarbon.	Viscosity in cs. at—		Ratio of V_0 to V_{100}.
	0° C.	100° C.	
n-Heptane . . .	0·743	0·320	2·3
n-Decane . . .	1·742	0·5335	3·3
n-Hexadecane . .	7·848	1·288	6·1

The table shows that characterizing a liquid by the viscosity–temperature slope (on a logarithmic scale) does not necessarily tell us much about its class, except when we work in the same viscosity range (cf. reply to Mr. Hyde).

These remarks apply to the study of so-called "perfect" oils. Two "perfect" oils need not be of similar quantity if they differ in viscosity value, if by "quality" we mean belonging to certain families of compounds showing certain similar characteristics. As performance of an oil is not merely a function of the viscosity, but also of such factors as chemical stability, it is believed that characterization factors such as the V.I. may be more useful than the viscosity–temperature slope. This statement is

based on the assumption that the basis of the V.I. included considerations other than viscosity temperature coefficients in choosing the H and L series oils.

With regard to low values of v_2 giving peculiar V.I. values, the present paper was intended to be limited to 2 cs. at 210° F. If $v_2 = 1$ cs., n is of course infinite, and V.I. from equation (11) becomes negatively infinite. However, this difficulty is only apparent, due to division by zero. If the unit of viscosity is made 0·001 stoke, $\log v_2 = \log 10$ m.s. $= 1$. Of course, the constants have to be adjusted to give a V.I. on the same scale as that obtained from the "centistoke scale." In the present paper we did not consider it necessary to extend the V.I. scale to lower values than 2 cs. at 210° F. chiefly because for such oils we do not recommend measurement of viscosity at 210° F. for V.I. purposes. Instead we hold the view that a V.I. number should be calculated from measurements made at lower temperatures. As indicated in the paper, we are endeavouring to extend the modified V.I. system proposed in the paper, so that a V.I. value can be calculated from viscosity measurements at lower temperatures for thin oils which would be of identical significance as the V.I. calculated from 100–210° F., but which would not suffer the inherent errors of measurement at, or extrapolation to 210° F. As indicated in the paper consideration is also being given to extending the V.I. scale to cover all petroleum products. Pure liquids are at their boiling points when their viscosities are between 0·3 and 0·5 cs.

THE PROBLEM OF ENGINE DEPOSITS.

By A. Lahiri, Ph.D., M.Sc., D.I.C., M.Inst.Pet., Fl./Lt. Z. Karpinski, Inz. Chem., and E. W. J. Mardles, D.Sc., F.R.I.C. (see pp. 271–302).

This paper was presented by Dr. Lahiri.

Mr. G. C. Gibbons said that with regard to the figures given in Table I, it seemed to him that if the axial ratio figures—increase and decrease—were correct, then the Staudinger relationship would not be expected to hold. One would expect every increase in molecular weight to be a linear function of the viscosity, and the axial ratio of the particles should also increase. The decrease would not give the expected lineaf increase.

Mr. E. A. Evans desired to ask Dr. Lahiri the size of the column which he used in adsorption and the quantities of material which he obtained for detailed examination. The authors had produced an apparatus both for doing the oxidation and for the measuring of the viscosity. That was a tremendous step forward.

To refer again to the General Discussion on Lubrication (*Inst. Mech. Eng.*, 1937, **2**, 261), Burwell and Camelford had plotted temperature against coefficient of friction and at a particular temperature, the coefficient of friction fell and finally rose when it ceased. Burwell and Camelford postulated that the thin film separating the metal surfaces must take the form of a plastic solid rather than of a viscous liquid and that upon further heating the melting point of this solid is reached with subsequent reduction of the coefficient of friction. By investigation of the coefficient of friction at these high temperatures they could get away from the so-called seizing

temperatures of which they had heard in the past, and would be able to look at the whole subject in a more logical way.

Dr. LAHIRI said that they had used thermocouples inserted at various points in the piston, and had selected that temperature range for their work on actual oxidation of the oils. Most of this work had been brought forward in another paper. The temperature at which an oil functioned in an aero engine was of the order of 200–300° C., and the fact must be faced that oxidation took place at that temperature. They had given two results in the present paper of oxidation at 200° C., and equivalent results were obtained in forty hours as at 235° C. in five hours.

The size of columns used had varied for different types of work. They had used a column 2 inches diameter and about 6 feet long, using various media, like activated silica and various other materials. For fractions obtained from the large-scale columns they had used, according to the quantity of the substance, columns of either 35-mm. diameter and 4 feet length, or 15-mm. diameter and 72 inches length.

If it was desired to do solid chromotography, which was much quicker, longer columns could be used.

COLONEL S. J. M. AULD stated that Dr. Lahiri and Dr. Mardles' paper was so extensive and so largely concerned with the theoretical and observational background of the tests which they proposed for use that he found it difficult to discuss it in the ordinary sense, nor did he propose to do so at the present moment. He wished, however, to express the opinion that the paper was very timely. With the adoption of engine tests for the evaluation of oils laboratory examination seemed to be slipping into the background. It had been fully realized, however, at the numerous conclaves to which Mr. Evans had made reference, that if the best were to be got from engine tests, examination of the used oil must be included, even if this did not lead to replacement of engine tests by laboratory procedure. The trouble was to know what to measure in the used oil. By approaching the subject logically the authors appeared to have broken fresh ground, and there seemed little doubt that the measurement of specific viscosity of the full suspension of the used oil, its behaviour when oxidizing at high temperatures, and its tendency to deposit were all observations capable of leading to an interpretation of oil and lubricating values. This development of new mechanism of appraisal at the present time might prove of inestimable value.

As regards the high-temperature viscosity determinations and the gelation noted, he pointed out there were other ways in which this phenomenon had been tackled. He had in mind the I.A.E. work recorded by McNicol, Williams, and Lamarque (*J. Inst. Petrol.*, 1939, **25**, 751), work which had recently been confirmed and extended in Moscow. In the former the shape of the curves measuring breakaway force against time were significantly similar to Lahiri and Mardles' curves, in that there was an increase to a maximum indicative of a complete change in nature of the oxidized film.

He looked forward to the development of the present authors' work, and asked particularly what was Dr. Lahiri's view of the possibilities of turning the tests described into routine examination which could be correlated with engine results on the bench or with practice.

DR. LAHIRI, in reply, said that they were not interested in the measurement of viscosity so much as what he might term the gel point; at higher temperatures there was no difference of viscosity.

There were two types of sticking—one the cold sticking when the engine stopped, but there was another kind of sticking which came after a certain temperature had been reached. The latter might well be correlated with this gel point of the oil under particular conditions of test.

MR. A. DE WAELE, in a written contribution, said it was a matter of regret that the Stormer results should have been returned from purely arbitrary points on the viscosity-shear lines, as the latter need not necessarily be similar in shape for different systems, the rate of change of these two parameters one with another being a function of the nature of the material under examination. More useful results would, in his opinion, have been obtained had the arbitrary points selected for viscosity been chosen where tan a approached to a zero value—*i.e.*, nearer to the asymptote to the curve. He was, in any case, unable to agree that the value of tan a at any point is a criterion of rigidity as distinct from mere non-Newtonian behaviour free from rigidity or yield value (see de Waele and Dinnis, *Physics*, 1936, **7**, 426–431).

In discussing the Newtonian character of suspensions in viscous fluids, the authors indicate the reason why the specific viscosity of sols is greater the greater the viscosity of the suspending medium, and attribute the cause to the longer time of orientation of anisodimensional particles when in the more viscous fluid. The statement appears ambiguous in view of the contrary evidence of some of the experimental results shown. He had observed many instances where suspensions of solids of equal concentration in fluids of low and high viscosity led to high and low rigidities, respectively. This, however, he attributed to the generally sympathetic agreement between viscosity and dispersive power, the former constant virtually following molecular complexity and hence dispersive power. A comparison of the rate of change of mobility μ (dv/dS) with increasing concentration of suspended phase (Prussian Blue) in, respectively, liquid paraffin and in oxidized oil of similar viscosity, shows the latter to exhibit a closer approximation to the theoretical Einstein line than does the non-dispersing paraffin. (de Waele, Symposium on "Wetting and Detergency," 1937, 65).

The slow rate of sedimentation and large sediment volume of suspensions showing high specific viscosity was suggested by the authors as being due to the slight rigidity of the oils. Interpreting this rigidity as being located about the individual particles of the sediment, this would lead *ipso facto* to large sediment volumes resulting from high rigidities, and not to greater thicknesses of so-called lyosorbed layers, as has been sometimes suggested. The mechanism of formation of such rigid layers, most evident in case of media of low polarity, offers a fruitful field for speculation and investigation.

DR. E. W. T. MARDLES, in reply, said Mr. de Waele is right in drawing attention to the arbitrary nature of the viscosity measurement and of tan α; these values depend on the conditions of measurement and on the dimensions of the viscometer, etc., but they do serve in a rough way to indicate when the oxidising oil passes from a true liquid to a suspension. His experiments with Prussian blue pigment in liquid paraffin and the more polar oxidised oil of similar viscosity are in tune with our findings of carbon

black suspensions. Our remarks on the effect of the viscosity of the medium on the specific viscosity were based on measurements in liquids of the same homologous series or with the same liquid at different temperatures.

The slight rigidity of oils, mentioned as a possible cause of the big differences found in sedementation rates and sediment volumes, is of course not the fundamental reason as Mr. de Waele points out. The main reason is the varying degree of flocculation which in turn is associated in some way with the lyosorbed layer.

LUBRICATING GREASES.

By A. S. C. Lawrence, Ph.D., F.R.I.C., F.Inst.Pet. (pp. 303–314).

This paper was presented by the author.

Colonel S. J. M. Auld said that Dr. Lawrence's observations on gelation were more precise and extended than anything of which he had heard. Also, the conception of the T_1 and T_2 temperatures had led, and were still further leading, to an elucidation of grease structure and manufacturing control.

He thought, however, that Dr. Lawrence was perhaps a little hard in his scathing reference to rule-of-thumb, our grandfathers, and the cookery book. Some war-time acquaintance with the cookery book had made him much more of an admirer of its precision than in the past, and he felt it compared quite favourably with laboratory manuals, or even synthetic manufacturing procedure in the repeatability of its results. It must not be imagined that all grease was used for the lubrication of colliery tubs or that all grease manufacture was spit-controlled or the raw materials measured out in Old Bill's cap. It would not have been possible by such means to develop and produce the E.P. greases which were pumped for hundreds of yards for the lubrication of modern strip steel mills or to the many thousands of bearings involved. It was interesting to note that such grease was frequently of the mixed-base type which Dr. Lawrence regarded as thoroughly bad procedure. Nor would it have been possible without considerable knowledge of what was going on to have produced in substantial tonnage those very calcium base greases of high melting point to which Dr. Lawrence had longingly referred. There was, in fact, a modern and high-grade side to this grease business wherein had been acquired considerable scientific knowledge of the processes and requirements. That side was appreciative of Dr. Lawrence's work and its implications. He hoped this valuable paper would lead to overt publication from other sources.

There were one or two individual points to which he wished to refer: firstly, he would tilt gently at Dr. Lawrence's criticism of the conception of calcium soap greases as emulsions of water-in-oil. He asked Dr. Lawrence what was the essential difference between this and peptization? As far as he understood, the latter, in this case, would represent a dispersing action effected by adsorption of the peptizing agent—*i.e.*, water, at the oil-soap crystal interface. Was there any difference between this and the apparently mirror-image effect of emulsion stabilization by adsorption of the soap at the oil–water interface? Both would result in stable distribution

of water within the oil. The unfortunate ease with which stable water-in-oil emulsions of small water content could be formed by contamination lent colour to the theory of the emulsion mechanism.

In the second place, he would like to underline everything Dr. Lawrence had said concerning the need for studying the effects of the individual fatty acids. Solubilities, transition temperatures, consistencies, heat stabilities, and so on varied markedly for different fatty acids with different bases, and to an appreciable extent also with different oils. Ultimately grease-making practice would undoubtedly be in the direction of controlling the fatty raw materials and their individual fatty acid content, and then making the necessary adjustments from other sources to ensure standardization. This could only be done if the behaviour of the separate fatty components were known.

In his opinion the question of out-of-standard raw materials was one of the biggest difficulties in practical grease-making. The other was the type of equipment in use. Temperature control in heating as well as cooling being of such paramount importance, it was unfortunate that there had to be such dependence on batch manufacture and separate kettles, even the best of which were bound to be of low efficiency in control. The reason doubtless was that there were too many different types and grades of grease in use. Continuous manufacture and continuously controlled cooling were consequently difficult to adopt. Perhaps with the limitations of numbers of greases to which Dr. Lawrence looked forward these things would alter, and there were already strong indications, particularly as regards cooling, that they would.

Dr. Lawrence, taking up the point raised by Col. Auld about the effect of water, suggested that some of that water was hydrolizing, and probably the most effective peptizer was the stearic agent. One could stabilize calcium stearate by adding a little free fatty acid, but he was not satisfied that the two were quite identical. It was impossible to make a stable calcium soap from any of the ordinary fatty acids without some water and without hydrolysis. Both in practice and in research work on the subject it was important to bear in mind that these soaps had a habit of showing serious instability.

Dr. Lahiri said that in his laboratory some experiments had been carried out in connection with the corrosion of the oil, and some preliminary work was done on the separation of copper stearates. It was found to be fairly easy; a quick method for industrial control.

Mr. Scott Blair asked to what extent electrical conductivity helped in eliciting the state of the emulsion.

Dr. Lawrence replied that the few cases which he had examined himself had not shown any electrical conductivity at all, but he did not think he had ever tried it on calcium soap greases.

Mr. D. L. Samuel said that he agreed that Dr. Lawrence had been hard on grease-makers. The old idea that grease was only used when one could not use oil was now somewhat out of date. He thought they must regard grease as being rather different from what it was thirty or forty years ago.

He was interested in the author's Fig. 1, although he wondered what was meant by Nujol. It appeared to him that this might be any white oil. According to this curve, at high temperatures the grease or soap/oil was a

liquid which on cooling to a certain temperature suddenly increased in viscosity and became a gel. Further cooling increased the viscosity of the gel until a point was reached when a sudden drop in viscosity occurred and a microcrystalline paste was formed. The author concludes from this "so we can expect that a grease shall lose consistency at low temperature and on heating become suddenly more viscous."

He did not know what the author meant by consistency, whether it was A.S.T.M. penetration or some form of viscosity measurement, but in his experience normal greases did not increase in consistency with increase in temperature. This phenomenon was encountered, however, with aluminium stearate greases and perhaps was a function of greases made with more or less pure soaps.

DR. LAWRENCE: Yes, that is so.

MR. SAMUEL further asked whereabouts commercial grease came in Fig. 1. Was it somewhere between T_1 and T_2, or below T_2?

He also wished to join issue with Dr. Lawrence when he said that soap was the important factor in the formulation of a grease and that the mineral-oil base was much less important. He strongly disagreed with that. Anybody who had tried to make up commercial greases would find that there were great differences in the structure of greases according to the type or oil used, and one could get oils which would not yield a satisfactory grease at all. Thus, highly refined oils might be very unsatisfactory for grease-making.

Dr. Lawrence had said that the mixing of metals in grease-making was not satisfactory. But mixed-base greases had been used with success for many years, and such greases were preferred by some users. There was the question also of syneresis. This depended very largely on the viscosity of the oil base. It was more pronounced with a fluid oil than with a highly viscous medium. Troubles due to "bleeding" were nearly always confined to greases made with the thinner oils. He did not agree that greases should be regarded as sponges feeding oil to a bearing.

Although the author said that pure sodium stearate had never been isolated he had stated that aluminium tristearate, bistearate, and monostearate were available. He himself had never been able to get hold of these materials and he would like to know how to obtain them.

DR. LAWRENCE said that he had not stated that these stearates were available; what he had said was that aluminium tristearate could be made easily, and so it could—if one knew the right way!

In the ordinary way the calcium soap greases would be below his T_2 in Fig. 1. He still stuck to his statement that the effect of the oil was much less serious than the effect of soaps.

COL. AULD said that E.P. greases in steel mills were mixed base greases—lead and calcium.

DR. LAWRENCE added that he had been very glad to hear the previous speaker declare his belief in grease lubricating as grease. He believed in that as well. He regretted it if he had been considered too rude about "grandfather and Mrs. Beeton."

MR. H. L. WEST said that he had often thought that the effect of water in anhydrous soap was largely to shift the transition stage. It appeared to him that precipitation occurred round about a certain temperature, and

that the effect of water was to stop precipitation and to give either a colloidal or some other solution.

Concerning the point made by Mr. Samuel about mineral oil, it seemed that mineral oil could play a remarkably important part in grease structure. It was possible to peptize soap solutions with soluble material. It was said that soap in ethyl alcohol could be peptized by water; but surely the water was soluble in ethyl alcohol. Peptization was not as simple as it might appear to some people, and he himself had doubts about it. He was convinced that the rate of cooling of the grease could exert a remarkable influence on the final structure. What was done to stop crystallization was to add a plasticizer. He had often thought that peptization might be a plasticizing effect. He had been very much interested to hear Dr. Lawrence say that the soda base greases were between T_1 and T_2 in his diagram.

Dr. Lawrence said that he did not think too much could be affirmed concerning the behaviour of soaps in the presence of water. As for peptization, a peptizer was a substance which in small quantities increased the dispersion of substances in a dispersing medium. That covered everything. He did not think that he had said that a peptizer must be insoluble.

Dr. E. W. J. Mardles desired to mention an experiment carried out recently at Farnborough. Following up some work done by Gulley and Puddington of the National Research Council in Canada, a few grams of powdered sodium stearate were dropped into an oil and its volume measured at different temperatures. They found that in swelling the soap took up a certain amount of liquid increasing slowly in volume until a temperature of 75° C., corresponding to the first melting point, was reached, from which point it began to swell more rapidly. If water, glycerol or other plastizer were added the swelling was first of all increased and the temperature of the first melting point was reduced. Calcium, magnesium and other soaps swelled to large amounts; magnesium stearate had high swelling, sodium stearate the lowest.

Dr. Lawrence agreed that the swelling effect deserved more investigation.

Mr. E. A. Evans said that he was emboldened to say one word in defence of the first paragraph of Dr. Lawrence's paper, which seemed to have caused a little criticism. He himself accepted a certain amount of responsibility for that paragraph; the author and he had wondered whether it might call forth the comments which it had. He supported Dr. Lawrence in what he said about "cookery-book stuff."

Dr. A. H. Nissan said that peptization did not always imply subdivision, sometimes it implied coagulation. One could get some soluble lime soaps and if they were perfectly dry they have a clear liquid with hydrocarbons, to which one could keep on adding water to obtain at first a gel and then complete separation. Thus, gellation is produced not by subdivision of a large complex but by coagulating the small units of the solute into larger macromolecules using water as the linkage agent. Dr. Lawrence had very masterfully simplified a problem which was more complex than the casual reader of this paper might suppose.

Concerning the aluminium stearate, he had seen a reference to Dr. Lawrence's method of preparing the tristearate. One could deal with a sample of aluminium stearate in such a fashion that if the material were ashed it

gave one a monohydroxy-distearate. In fact it was a mixture of the monohydroxy-distearate plus the dihydroxy-monostearate plus a little loosely attached free stearic acid.

He wondered whether the case of the tristearate had been studied with the object of discovering whether the three stearate groups were attached chemically, so that it might be called a chemical compound and not a loose association of the third stearate group to a monohydroxy distearate soap.

DR. LAWRENCE mentioned that an aluminium tristearate was the easiest made of all the aluminium soaps. One just added the fatty acid. Aluminium stearate did form gels, just like other stearates.

MR. S. R. PETHRICK suggested that Dr. Lawrence should study soaps in oil with rapid cooling instead of slow cooling. In view of the introduction of lithium soap greases, rapid cooling technique was becoming important.

He had once heated sodium stearate plus a little caustic soda with Pool 97 (Special) oil to 200° C. and rapidly chilled the product. A mass of crystals and free oil was obtained. On raising the temperature to 250° C. instead of 200° C. a grease having a melting point above 200° C. was obtained.

MR. WEBBER said that if a grease was taken above T_1 in Fig. 1 an entirely different structure resulted. It would appear that some plasticizer or peptizer was required to ensure that the grease would not regain the coarse fibrous structure in service.

The difference between an oil and a grease lay in two points. The grease possessed a yield value which the oil did not, in that the grease could maintain the film whereas the oil would continue to flow with any stress, however small. This property could be and had been used successfully, and it was manifested whether water was present or not.

A grease should have a small yield value at low temperature and a large yield value at high.

COL. S. J. M. AULD, in proposing a vote of thanks to the authors of the various papers, congratulated the Institute of Petroleum and the British Rheologists Club on the great success of the combined meeting. He especially complimented the Chairman and Mr. Evans on the result of their work.

The vote of thanks was duly accorded, and the meeting terminated.